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SOL-GEL TECHNOLOGY FOR LOW-VOC, NONCHROMATED ADHESIVE BONDING APPLICATIONS

SERDP Project PP-1113, Task 1

James J. Mazza

Materials Integrity Branch (AFRL/MLSA)
Systems Support Division
Materials and Manufacturing Directorate
Air Force Research Laboratory, Air Force Materiel Command
Wright-Patterson Air Force Base, OH 45433-7750

Georgette B. Gaskin
U.S. Navy (NAVAIR)

William S. De Piero
U.S. Army (RDECOM-ARDEC)

Kay Y. Blohowiak
The Boeing Company (Phantom Works)

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AIR FORCE RESEARCH LABORATORY
AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750

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JAMES J. MAZZA
Team Lead
Adhesives, Composites & Elastomers Team
Materials Integrity Branch

MARY ANN PHILLIPS
Chief
Materials Integrity Branch
Materials & Manufacturing Directorate

GARY A. KEPPLE
Deputy Chief
Systems Support Division
Materials & Manufacturing Directorate

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James J. Mazza (AFRL/MLSA)
Georgette B. Gaskin, U.S. Navy (NAVAIR)
William S. De Piero, U.S. Army (RDECOM-ARDEC)
Kay Y. Blohowiak, The Boeing Company (Phantom Works)

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Materials Integrity Branch (AFRL/MLSA)
Systems Support Division
Materials and Manufacturing Directorate
Air Force Research Laboratory, Air Force Materiel Command
Wright-Patterson Air Force Base, OH 45433-7750

Naval Air Systems Command (NAVAIR)
Building 2187, Suite 2340A
48110 Shaw Road, Unit 5
Patuxent River, MD 20670-1906

The Boeing Company, Phantom Works
P.O. Box 3707, MC 73-09
Seattle, WA 98124-2207

U.S. Army, RDECOM-ARDEC
Building 355
Picatinny, NJ 07806-5000

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Air Force Research Laboratory
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Wright-Patterson AFB, OH 45433-7750

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14. ABSTRACT
A government-industry team, primarily funded by the Strategic Environmental Research and Development Program (SERDP) under Project PP-1113, developed new environmentally friendly metal surface preparations for adhesive bonding applications. These processes were based on waterborne, nonchromated chemistry developed by Boeing and designated Boegel-EPII. Preparation of aluminum, titanium, and stainless steel adherends was investigated for on-component repair as well as original equipment manufacturer (OEM) applications. The bulk of the work was conducted to establish pretreatment steps for cleaning, deoxidizing, and roughening metal surfaces. Multiple viable approaches, varying in degree of effectiveness and complexity, were developed. Sol-gel chemistry application processes were also investigated as were post-treatment priming operations. Surface characterization efforts and kitting studies for the multicomponent sol-gel chemistry received significant attention. Performance of surface preparations was primarily evaluated by means of the wedge test, although many additional tests were conducted, on several epoxy-based film and paste adhesives. The best processes developed, utilizing alumina grit-blasting pretreatment, are quite robust and yielded excellent bond strength and moisture durability results, rivaling the best existing practices. Variations using nongrit-blast approaches outperformed many approved repair processes. Government and industry organizations have begun to implement the new sol-gel processes for aluminum, titanium, and steel adhesive bonding applications.

15. SUBJECT TERMS
sol-gel, adhesive bonding, wedge test, aluminum, titanium, steel, surface preparation

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TABLE OF CONTENTS

PREFACE

This report documents the primary task of Strategic Environmental Research and Development Program (SERDP) Project PP-1113 (technical effort from January 1998 through September 2002). Secondary tasks are only mentioned, with references provided for further information. The work described herein pertains to the development of metal surface preparations, based on sol-gel technology, for adhesive bonding applications. This report contains nearly all of the technical data from Project PP-1113 that relate to processes likely to be implemented by Department of Defense (DoD) and other organizations. A follow-on effort, Environmental Security Technology Certification Program (ESTCP) Project PP-0204, addresses transition issues required to implement the new sol-gel metal bonding surface preparations.

Project PP-1113 was a large team effort primarily funded by SERDP. Many individuals from government and industry organizations contributed both to the success of the project and the writing of this report. The SERDP co-Principal Investigators were Jim Mazza of the Air Force Research Laboratory (AFRL/MLSA at Wright-Patterson AFB, OH) and Georgette Gaskin of the Naval Air Systems Command (NAVAIR at Patuxent River, MD). Bill De Piero (RDECOM-ARDEC at Picatinny, NJ) was the Army representative, and Kay Blohowiak of the Boeing Company (Phantom Works in Seattle, WA) was the key industry team member. The above individuals were the primary authors of this report and led working groups that developed the data contained herein. Dan McCray from the University of Dayton Research Institute (UDRI) also contributed significantly to the report.

Other team members included the Department of Energy (DOE) representative, Jim Tira of the Honeywell Corporation, Bill Trzaskos of Cytec Engineered Materials, Inc., and Stephane Pyrek of Advanced Chemistry & Technology. Paul Hauwiller of the Anteon Corporation coordinated team activities and played a significant role in formatting the report.

Project PP-1113 participants from NAVAIR included Andy Guy and Justin Stayrook at Patuxent River as well as the Naval Air Depot representatives: Don Knapp (Jacksonville, FL), Bill Alexander (Cherry Point, NC), and Doug Perl and Don Harmston (North Island, CA). Boeing support was provided by Ron Stephenson, Rob Anderson, Ken Krienke, Michele Ricks, Joe Osborne, and Don Sekits. Technical data were generated for AFRL/MLSA by Dan McCray and Jeff Smith of UDRI, supported by Kylie Huber and Carly Wreesman of the Southwestern Ohio Council for Higher Education (SOCHE). Warner Robins Air Logistics Center (WR-ALC) representatives, Jay Fiebig and Bill Schweinberg, provided input and data pertaining to Air Force applications for sol-gel metal bonding surface preparations.

Vince McGinniss and Steve Risser of Battelle and Henry Zheng of Chemat Technology, Inc. were team members who contributed to PP-1113 efforts that are not documented in this report.

EXECUTIVE SUMMARY

The Strategic Environmental Research and Development Program (SERDP) funded a team to develop surface preparations utilizing sol-gel technology for adhesion to aluminum, titanium, and steel. This SERDP Project PP-1113 effort primarily focused on development and optimization of methods for preparing metal surfaces for adhesive bonding with epoxy adhesives. The goals were to design processes that 1) use environmentally friendly materials, 2) increase durability, 3) improve process robustness, 4) decrease repair time, 5) use simple equipment, and 6) increase affordability. Personnel from Air Force and Navy depot sites were involved in the requirements generation and testing cycle to ensure end-user needs were met.

The main technical task developed prebond surface preparations based on a specific waterborne sol-gel chemistry, Boegel-EPII, that had been developed previously (in part by SERDP Project PP-130). Little was done to change the sol-gel chemistry. However, significant work was accomplished to establish pretreatment and application procedures. Processes that involved grit-blasting as part of the surface activation and those that employed alternate abrasion techniques were investigated. Both field-level and depot/production adhesive bonding operations were addressed. Testing was conducted to establish operating windows for the various process steps, and options were defined for many steps. The wedge test (ASTM D 3762) was mainly used for screening, but significant additional testing was conducted.

The grit-blast/sol-gel procedures, including application of a waterborne, chromated primer, produced bond strength and moisture durability performance equivalent to those obtainable using the best existing treatments for aluminum, titanium, and steel alloys. Excellent strength and durability performance were also demonstrated for nongrit-blast alternatives, particularly for aluminum bonding using both film and paste adhesives. These processes, including the use of primer via brush-on application, typically outperformed the currently qualified processes employed for field-level bonding while reducing hazardous material usage and processing time.

Secondary PP-1113 efforts were aimed at 1) hybrid coating development, 2) sealant adhesion, and 3) molecular modeling. Hybrid formulation was intended to completely eliminate hexavalent chromium from prebond preparation by combining sol-gel chemistry and nonchromated bond primer in one step. The sealant work focused on titanium adhesion in a production environment, since this was seen as a need when the project commenced. Although the hybrid coating showed some feasibility and the sealant adhesion task yielded good results, further effort is not planned in these areas. The hybrid coating requires extensive additional work, and alternate waterborne adhesion promotion approaches have been found for sealant applications. The molecular modeling task provided some insight but did not add significantly to overall process understanding. The secondary efforts are not discussed in this report, however, the hybrid and sealant work are documented elsewhere[1,2].

After completion of transition work intended to address issues pertaining to end-user environments, it is almost certain that multiple variants of the new technology will be implemented for both military and commercial aircraft applications. Limited implementation has already occurred for aluminum, titanium, and steel applications. The sol-gel formulation that is the key to the new surface preparation processes, Boeing's Boegel-EPII, is now commercially available in kit form as AC-130 from AC Tech in Garden Grove, CA.

1 INTRODUCTION

1.1 Objective

The primary objective of Strategic Environmental Research and Development Program (SERDP) Project PP-1113 was to utilize sol-gel technology to develop surface preparation processes for aluminum, titanium, and steel alloys. This project focused on the development of user-friendly methods for preparing metal surfaces for bonding with epoxy adhesives. A secondary objective was to improve adhesion of sealants to metal surfaces. The goals of the project were to design processes that 1) use environmentally friendly materials, 2) increase durability, 3) improve process robustness, 4) decrease repair time, 5) use simple equipment, and 6) increase affordability. The new processes developed were intended to reduce or eliminate the volatile organic compounds (VOCs), chromates, and strong acids/bases typically found in metal surface treatment and priming steps conducted for adhesive bonding. Reductions in both hazardous wastewater streams and grit-blasting associated with existing processes were also sought as was improved bonded joint performance.

1.2 Problem

State-of-the-art metal surface preparations for adhesive bonding mainly consist of anodization or etching processes using strong acids or bases. Many of these also contain hexavalent chromium, and associated rinsing steps generate contaminated wastewater. Surface treatment is generally followed by application of a corrosion-inhibiting adhesive primer that typically contains high VOC levels and hexavalent chromium. Cytec Engineered Materials' BR 127, the industry standard adhesive primer, contains approximately 780 grams/liter VOC and strontium chromate at 10-12% of the total solids weight.

In recent years, many federal and state regulations have set strict limits to regulate (eliminate or minimize) the use of hazardous materials and associated waste. In Southern California, VOC emissions are a particular concern. In other states, such as Florida, groundwater contamination is of great interest, so processes generating chromated wastewater are restricted. Many regulators, including the Federal Government, are legislating limits for hazardous air pollutants (HAPS). In order to meet or exceed these legislative targets and be "good citizens," many commanders of Department of Defense (DoD) field units have banned or severely restricted the use of chromates and VOCs at their installations, improving the environmental conditions and potentially adversely impacting mission readiness.

As a result of the new regulations and increased costs of hazardous waste disposal as well as increased awareness and cost associated with employees' health and safety, it is imperative that low-VOC/nontoxic surface treatments/primers be developed for structural adhesive bonding applications. At the same time, performance cannot be adversely affected by implementation of new processes since this would impose unacceptable safety, readiness, and/or cost penalties.

An additional problem that complicates implementation of new processes is the fact that common requirements do not exist for prebond metal surface preparation. Military specifications are nonexistent, and manufacturers use their own processes and documents.

Changes to the existing processes in the DoD must typically be made on an individual weapons system basis since there is really no way to globally enact a new procedure.

1.3 Background

1.3.1 Metal Surface Preparation

Surface preparation is essential for the successful implementation of adhesive bonding technology. Both the initial bond strength and the subsequent bond durability are critically dependent on the interaction between the adhesive (and/or primer) and a pretreated adherend surface. For metals, surface preparation involves both the removal of weak boundary layers or layers that are chemically incompatible with the adhesive and the formation of stable, adherent layers that are mechanically and chemically compatible with the adhesive[3].

Initial adhesion is easier to achieve than long-term durability in the service environment. For metal bonding, particularly on aluminum, resisting the attack of moisture is the key to long-term durability. Eventually, moisture will gain access to the interface region between the polymer and metal. Once there, it can destroy bonds based on weak chemical or physical attractions, such as hydrogen bonds, and it can cause unstable oxide layers to further hydrate, thereby destroying the metal surface to which the polymer is bound. To achieve initial adhesion, contamination and weak native oxide layers must be removed from the metal surface. Adhesion is improved if the surface is roughened, particularly at the microscopic level. To achieve long-term moisture durability, a stable surface layer must be created and moisture access to the metal-polymer interface region must be minimized.

Pretreatment steps are a critical part of the overall surface preparation process. These steps remove contamination and the existing oxide. They also can play a role in roughening the surface. Application of a corrosion-inhibiting adhesive primer (CIAP) is a typical post-treatment step employed when long-term durable bonds are desired.

1.3.2 Current Prebond Surface Preparation Processes

There are many qualified surface preparations for metal adhesive bonding. Different treatments are typically required for different metals, such as aluminum, titanium, and steel. Several processes exist for each metal, and additional variants are required for on-component processing, as opposed to immersion tank (tankline) processing. The best treatments yield excellent long-term moisture durability. However, these processes tend to involve hazardous chemicals and may not be viable for some applications, such as on-aircraft repair. Many approved processes, especially those for repair, do not deliver good durability or even acceptable initial adhesion.

In a production or depot setting, facilities are generally available for tankline processes. These include anodization and etching procedures using strong acids or bases. For aluminum, phosphoric acid anodize (PAA) used with a corrosion-inhibiting primer is the premier treatment, offering good adhesion and durability performance. After degreasing using solvents or aqueous cleaners, the native oxide layer is typically removed via acid etching. The anodize process requires an electrical current and grows a controlled aluminum oxide layer with a specific morphology from the base metal. Adhesion is primarily obtained when the polymer (adhesive or primer) penetrates the very fine pore structure of the anodic film. Other acid anodization

processes available for aluminum treatment include: chromic, sulfuric/boric, and thin sulfuric. Acid etches, such as the various sulfuric acid/sodium dichromate processes, create morphologies on aluminum surfaces without the use of electrical current. However, the structures obtained are typically not as robust as those achieved by anodization and do not provide the same level of interlocking for polymers within the pore structure. Anodizes and etches are also common for titanium, with many including hydrofluoric acid. Acid etches are available for steel treatment.

In a repair environment, particularly on-component, surface preparations that provide acceptable bond performance are inconvenient or impractical to use. Adaptations of anodize and etch processes have been made, however, these typically are not conducted within optimal processing parameters and are much more difficult to apply. The hazardous materials (strong acids/bases and chromates) are harder to control and can be detrimental to the surrounding structure and personnel. Simple clean and abrasion processes are often employed, with a significant reduction in performance, particularly moisture resistance. The grit-blast/silane (GBS) process eliminates the acids but is time consuming (6-8 hours) and requires inconvenient heat cure and grit-blasting steps.

New prebond surface preparations are required for repair bonding of aluminum, titanium, and steel to reduce the use of hazardous materials, improve performance, and decrease costs. New processes are also required for production bonding of titanium and steel. Titanium applications employ hazardous chemicals such as chromic and hydrofluoric acids that are becoming difficult to use under current regulations. Current processes for steel use hazardous chemicals and do not typically provide exceptional performance.

1.3.3 Assessing Surface Preparation Performance

Since there are no common requirements or specifications for metal surface preparation for adhesive bonding, there is no one set of tests established to assess performance. The performance requirements can vary between users and even by application for an individual user. In all cases, the surface preparation should be evaluated with the rest of the bonding system for that application, including the metal alloy, adhesive, and primer. Strength tests, both static and fatigue, are generally required, with consideration given to the service temperature extremes. The most difficult parameter to measure is the most important: the ability of the surface preparation to provide long-term moisture resistance. There are no accelerated laboratory tests that can quantitatively correlate bond performance with service life. The wedge test (ASTM D 3762)[4] is probably the best available method for assessing moisture durability when it is used to make comparisons between new processes and fielded procedures with known service history. However, there are no standard conditioning parameters or pass/fail criteria for the test.

1.4 Approach

1.4.1 General

To develop new metal surface preparations that reduce the use of hazardous materials in adhesive bonding applications, this project built on previous work using sol-gel technology to deposit thin organic-inorganic coatings on metal surfaces in order to develop good adhesion between the metal and subsequently applied polymers (primer or adhesive) via what is believed to be a direct chemical bonding mechanism. The effort extensively leveraged previous research

conducted under SERDP Project PP-130 that developed a specific sol-gel formulation for adhesive bonding applications. The overall PP-1113 project was divided into four technical tasks: 1) optimization of sol-gel surface preparations for adhesive bonding of aluminum, titanium, and steel using a traditional approach wherein the sol-gel coating is followed by application of an adhesive primer (or left unprimed); 2) development of a hybrid coating in order to eliminate the separate priming step for bonding applications; 3) evaluation of the nonchromated, zero-VOC hybrid coatings as replacements for existing primers used with the current PAA prebond surface preparation for aluminum; and 4) leverage of the adhesive bonding work for sealant adhesion applications. The first task was by far the largest and most important part of the work. The second task, hybrid coating development, was seen as high risk but with the potential to further reduce the use of hazardous materials and improve performance for on-component bonding in the field environment. The third task, envisioned as a very small evaluation effort to be conducted if Task 2 was successful, was not conducted. The sealant adhesion task was also a small part of the overall effort. Only Task 1 is discussed in this report.

1.4.2 Sol-Gel

Sol-gel is a contraction for solution-gelation and refers to a series of reactions where a soluble metal species (typically a metal alkoxide or metal salt) hydrolyzes to from a metal hydroxide. The soluble metal species can also contain organic constituents that can be tailored for a certain application. The metal hydroxide functionalities condense to form an inorganic or organometallic polymer. The term sol-gel represents a very broad technology area. Solution chemistry possibilities are virtually limitless. Process variables can also be adjusted to obtain desired results. The technology is very flexible and tailorable. Brinker and Scherer provide a good sol-gel technology review[5].

Sol-gel technology is nearly 70 years old, with most early applications involving the deposition of inorganic thin films. In the last 15 years or so, sol-gel has been studied for surface treatment of metals for the purpose of promoting adhesion of polymers (adhesives, primers, coatings). In these cases, organometallic solutions are used. For the purposes of SERDP Project PP-1113, sol-gel technology was used to deposit an inorganic/organic thin film from solution onto a metal substrate. Sol-gel technology can provide a unique approach for forming chemical network structures to enhance bonding at metal interfaces. By carefully controlling the formulation chemistry and processing, gradient coatings can be formed with one side of the structure designed to contain appropriate functionalities to bond with the metallic substrate and the other side having organic functionalities that bond with a polymer (Figure 1.4-1). The solution chemistry and processing variables can be adjusted to achieve optimum properties. The chemistry, morphology, and thickness of the deposited film are tailored. This can lead to different formulations or processes for different applications in order to achieve optimal results.

Significantly different sol-gel chemistries from Boeing and Chemat Technology, Inc. were evaluated in the overall SERDP PP-1113 project. Boeing's waterborne formulation, Boegel-EPII[6], includes zirconium and silicon as the inorganic constituents (Figure 1.4-1) and is acid-catalyzed with a pH above 4. Boegel-EPII is quite reactive and must be used within a short period of time after mixing. This enables the coating to cure at ambient temperatures without additional heat or energy applied. Since it can be mixed from multicomponent kits and spray or brush applied, shelf stability of the mixture was not a concern. Due to its superior performance

in Project PP-130, Boegel-EPII chemistry was the primary focus of the major task in this project. Chemat's chemistry, Al 9201, is based on aluminum alkoxides in water with silane molecules providing the active organic functionality[7]. The inorganic components, therefore, are aluminum and silicon as opposed to zirconium and silicon. Chemat's formulation has a basic pH (around 10). The Chemat sol-gel chemistry has shelf life of about 6 months. Due to its stability and pH, Al 9201 was mixed with waterborne primers as part of the hybrid development task. Work associated with this task is reported elsewhere[1].

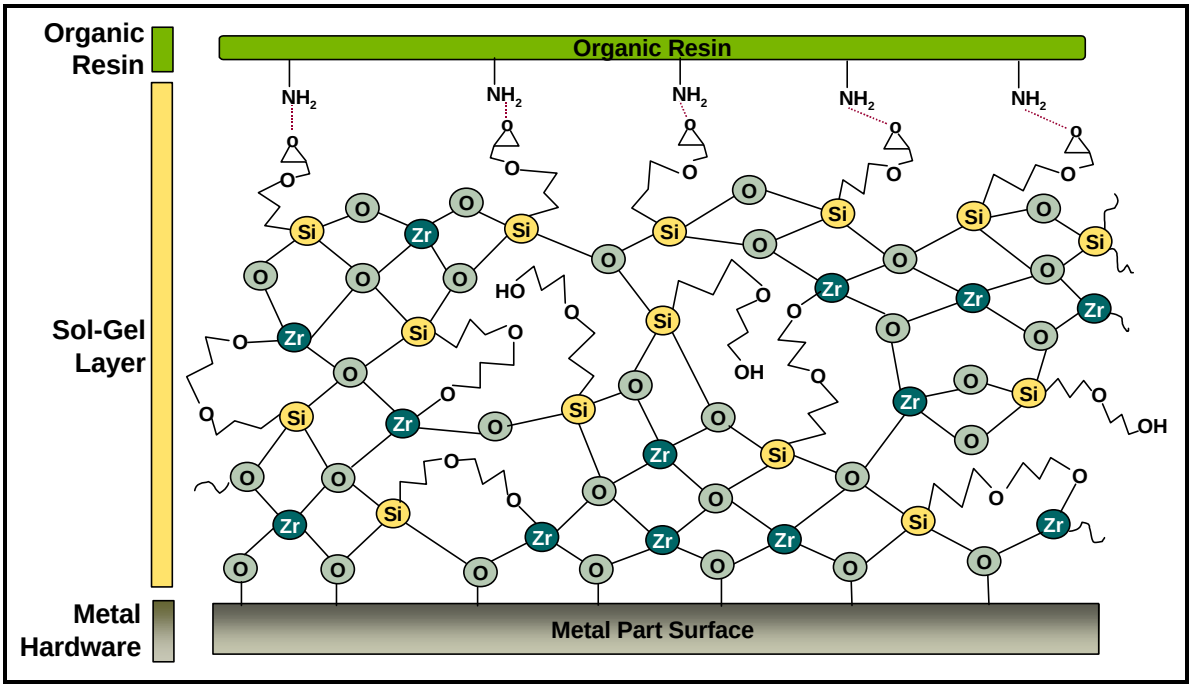


Figure 1.4-1: Notional Schematic of Boeing Sol-Gel Interaction with Polymers and Substrates

1.4.3 Program Structure

The sol-gel development effort involved the Air Force, Navy, Army, Department of Energy (DOE), and industry in a cooperative manner. The team structure, showing technical task responsibilities and relationships, is illustrated in Figure 1.4-2. The Air Force served as the focus for development for aluminum substrate applications, the Navy for titanium, and the Army for stainless steel. Boeing served as the technology integrator for the team and led the hybrid coating and sealant adhesion work[1,2]. Chemat hybrid work (not reported herein) was conducted through a subcontract with Boeing. Battelle (modeling), Cytec (primers), and DOE (analytical) efforts supported the development on all three metals. The Battelle work is not documented in this report. Advanced Chemistry & Technology (AC Tech) was the commercial supplier for Boegel-EPII kits, under their product designation AC-130, and also worked kitting issues. In addition, the Air Force, Navy, and Army representatives maintained open communication with their respective maintenance organizations to initiate limited field trials and enhance transition.

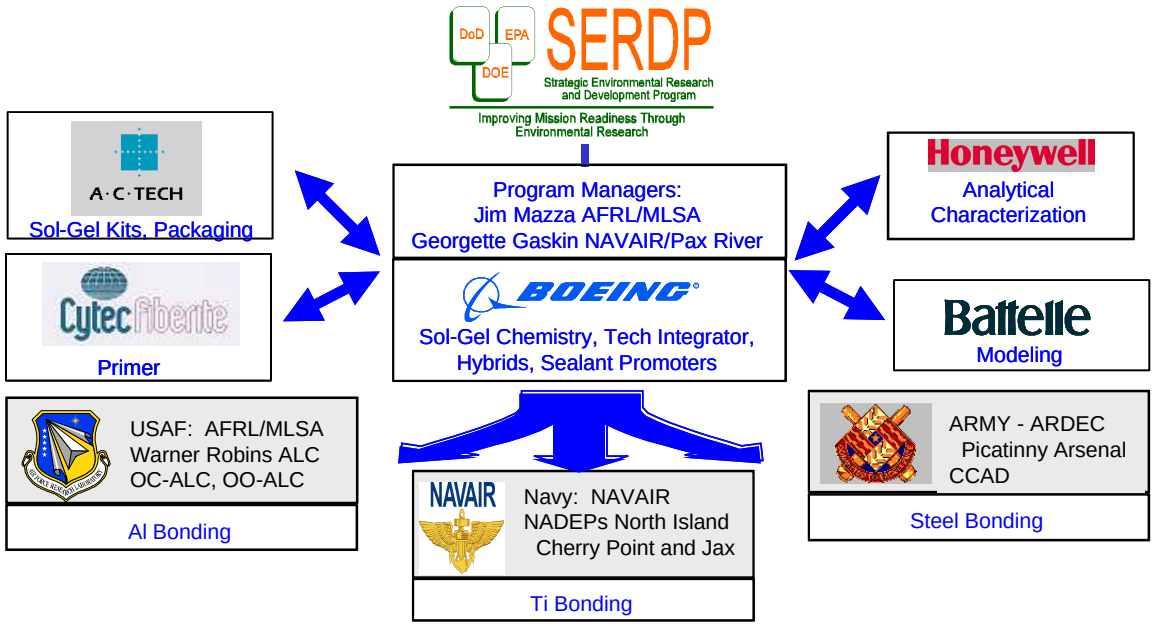


Figure 1.4-2: SERDP PP-1113 Program Structure

The primary focus of the project was to develop processes using Boegel-EPII to treat aluminum, titanium, and steel substrates for adhesive bonding. Development of pretreatments, sol-gel application procedures, and priming steps made up the bulk of the effort. This was accomplished by investigating the limits of the processing parameters for various bonding systems, primarily using epoxy film and paste adhesives. For the most part, coupon testing was used in an empirical fashion to determine optimal process conditions.

The wedge test was the principal means employed for the evaluations since bond moisture durability was of greatest concern. Environmental conditions for the test were either 120°F & 95-100% relative humidity (RH) or 140°F & 95-100% RH. Typical exposure times were 28 days, but longer tests were also conducted. Although crack growths were measured over time and minimal growth was desired, pass/fail was based on the failure mode of the opened specimen after conditioning. For the purpose of this program, a successful bond was one that exhibited at least 90% cohesive failure (within the adhesive layer). Failure modes from 95% to 100% cohesive were considered ideal. Adhesional failures involving the sol-gel coating were least desirable. These were failures at the interface between the sol-gel coating and the metal or the sol-gel coating and the polymer (primer or adhesive). These types of interfacial failures are often called “adhesive” failures. This term can be confusing since it does not refer to a failure of the adhesive, so “adhesional” is used to describe them in this report. Failures within the primer layer or between the primer and adhesive were also considered nonideal. Failures within the sol-gel layer, if any existed, could not be readily identified due to the nature of the sol-gel coating.

2 ADHESIVE BONDING - ALUMINUM SUBSTRATES

Aluminum alloys are prevalent in aircraft structures across the services. The majority of the applications involve 2000 and 7000-series aluminum alloys. Aluminum oxidizes in air, and this surface oxidation must be removed prior to the application of the sol-gel solution. In addition, corrosion protection methods must be employed to ensure that the potential for oxidation after bonding does not degrade the bonded surface and limit bond durability. This section discusses efforts to understand the processing parameters/windows and efforts to verify stable processes for aluminum using both grit-blast and nongrit-blast surface activation methods, primarily for repair applications. Evaluations were often conducted using nongrit-blast surface activation methods since these are typically more sensitive than grit-blast to process variations. In addition, both film and paste adhesives were included in the effort since they may respond differently to surface preparation process changes. Film adhesives typically cure at elevated temperatures and result in more consistent bondline thicknesses. Paste adhesives that can cure at ambient temperatures are required for many applications but may not "wet" the adherend surface in the same way as films that reach much lower viscosities during elevated-temperature cure.

2.1 Testing and Materials

A number of materials and processes were evaluated during this effort. In most cases, the details for the processing associated with the evaluations are given for each test. At times, full details for parameters held constant are not provided. Unless otherwise noted, test results are the average of 5 specimens taken from one bonded 2024-T3 bare aluminum panel. Grit-blasting was conducted with 50 micron (#280) or 80 micron (#180) alumina. The term "nylon pad" is used throughout as generic for 3M Company Scotch-Brite™ or equivalent abrasive media. Abrasive papers are often referred to as "sandpapers" even though grit was SiC, Zr O_2, or Al_2O_3. Early work with these materials, prior to identification of the best products, resulted in less than optimal performance. Unless otherwise stated, the basic Boegel-EPII formulation was used for all tests. It was either mixed from new chemicals in the laboratory or from kits supplied by Boeing or AC Tech. Treated surfaces were kept wet with sol-gel solution for between 2 and 3 minutes. Cytec BR 6747-1 waterborne, chromated bond primer (20% solids) was used, unless otherwise indicated. For baseline specimens, the primer was applied to a nominal thickness of 0.1-0.3 mil (0.0001-0.0003 inch), dried for 30 minutes at ambient temperature, and cured for 60 minutes at 250°F in an air-circulating oven. Alternatively, primer cocure with the adhesive was often conducted after the 30-minute air dry. The primer was spray applied using a conventional air spray gun (Binks Model 105) or a High Volume Low Pressure (HVLP) spray gun (Binks Model M1-G). Baseline specimens were bonded with 3M Company AF 163-2M (0.06 pounds per square foot (psf) areal weight) modified epoxy film adhesive cured in an autoclave for 60 minutes at 250°F under 35-45 psi. In some cases, the adhesive used was the one-side tacky version, but this is not separately noted. The wedge test was conducted either at 120°F or 140°F, depending on the parameters being evaluated. Nylon-pad/sol-gel preparations typically involved cocured primer and wedge test conditioning at 120°F.

2.2 Grit-Blast Surface Activation

Grit-blasting is a key component of many metal surface preparation processes. Grit-blasting removes existing oxide layers while creating a rough surface morphology that is conducive to

bonding. In addition, organic contaminates are easier to detect optically on grit-blasted surfaces, thus providing a good quality control measure during the surface preparation. Experience obtained during grit-blast/silane (GBS) development[8] led to the choice of grit-blasting as a logical surface activation step for use with Boegel-EPII to obtain desired bond performance.

To optimize the process parameters involved with activating the bonding surface and subsequent application of Boegel-EPII and bond primers, a designed experiment was conducted to determine significant processing factors. Once identified, several smaller experiments were conducted to determine optimum operating windows for individual steps in the surface preparation.

2.2.1 Grit-Blast Designed Experiment

Several key processing factors for a grit-blast/sol-gel process using Boegel-EPII were evaluated via a designed experiment conducted using an L16 array. The evaluated processing factors are listed in Table 2.2-1. Aluminum alloy type, Boegel-EPII application method, Boegel-EPII wet time, Boegel-EPII dry method, Boegel-EPII dry time, and bond primer factors were all assessed using a matrix consisting of 16 wedge test panels.

Table 2.2-1: Grit-Blast/Sol-Gel Designed Experiment Processing Parameters

Factor	Parameter #1	Parameter #2
Alloy	Al 2024-T3	Al 7075-T6
Boegel-EPII application method	Spray	Brush
Boegel-EPII wet time	10 minutes	20 minutes
Dry method	nitrogen force	ambient dry
Dry time	1 hour	4 hours
Primer	BR 6747-1	none

Panels were primed with Cytec BR 6747-1 (cured according to the manufacturer's recommendations), when specified, and bonded with AF 163-2M for 60 minutes at 250°F and 35-40 psi. Primer was applied to a nominal thickness of 0.1-0.3 mil (0.0001-0.0003 inch). The specimens were then tested at 140°F and 95-100% RH. The failure modes (percentage of cohesive failure) of the specimens were used to calculate the significance of each factor using the design of experiments philosophy[9]. Anova analysis was performed on the results and a chart was plotted in order to distinguish the significance of each factor and interaction. All factors and interactions with a standardized effect greater than the 95% confidence limit were considered significant, as shown in Figure 2.2-1. Only the primer and sol-gel dry method factors were considered to be significant. The primer/dry method interaction was also significant. Best durability was detected in panels when they were force-dried with nitrogen and primed. All processing factors other than primer and dry method were considered insignificant, including sol-gel application method, sol-gel wet time, and sol-gel dry time. Most wedge test specimens with optimum processing conditions exhibited crack growth less than 0.25 inches with cohesive failure modes (within the adhesive layer) as shown in Figure 2.2-2. Although the failure modes were primarily cohesive in nature, small "nicks" of adhesional failure (at the metal interface) were detected at edges of many specimens. However, these nicks are difficult to detect visually in Figure 2.2-2 due to the small size. It was estimated that the area of these small nicks was roughly 5% or less of the specimen test area.

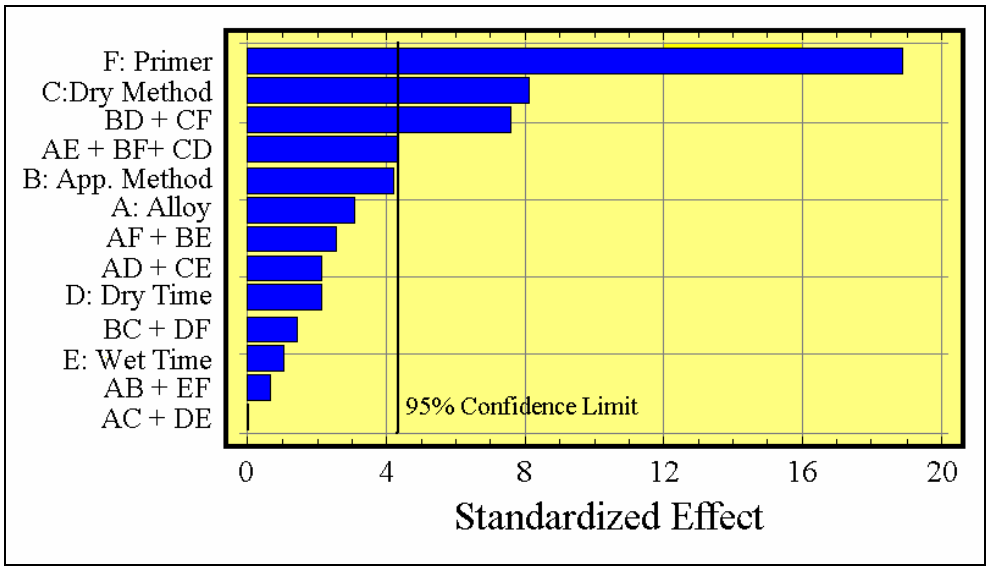


Figure 2.2-1: Significance of Processing Factors and Interactions for Grit-Blast/Sol-Gel Surface Preparation

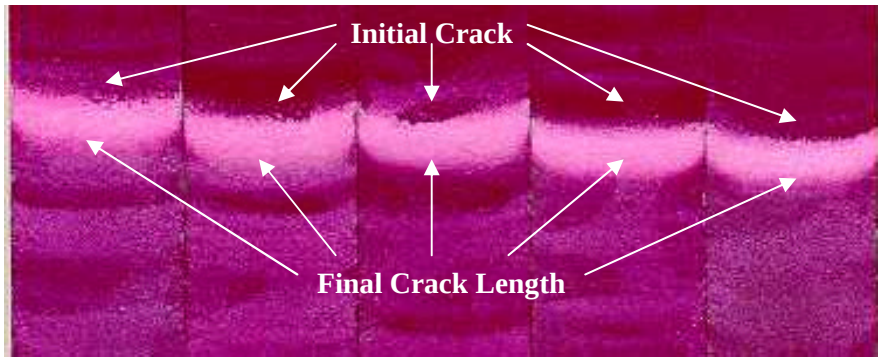


Figure 2.2-2: Cohesive Failure Mode Exhibited by Grit-Blasted Boegel-EPII Specimens with Optimum Processing Conditions

2.2.2 Effect of Aluminum Alloy

Although the grit-blast designed experiment (section 2.2.1) was unable to detect a significant difference between the performance results obtained using Boegel-EPII over grit-blasted surfaces on different alloys, a secondary experiment was conducted to verify this result. Grit-blasted wedge test panels were fabricated of bare Al 2024-T3, clad Al 2024-T3, and bare Al 7075-T6 adherends, treated with Boegel-EPII solution, primed with BR 6747-1, and bonded with AF 163-2M. Panels were machined into specimens, measured for bondline thickness and tested at 140°F and 95-100% RH. Results are show in Table 2.2-2. There appears to be no appreciable difference in either crack growth or failure mode due to alloy type.

Table 2.2-2: Effect of Alloy Type on Grit-Blast Wedge Test Results

Alloy	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
		1 hr	8 hr	24 hr	7 days	21 days	28 days	
Al 2024-T3 Bare	1.09	0.04	0.06	0.10	0.16	0.22	0.23	95% co
Al 2024-T3 Clad	1.22	0.01	0.07	0.11	0.15	0.23	0.24	96% co
Al 7075-T6 Bare	1.15	0.07	0.10	0.14	0.20	0.24	0.24	94% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.2.3 Boegel-EPII Wet Time Evaluation

In order to determine the effect of different Boegel-EPII wetting times, two experiments were conducted varying the Boegel-EPII wet time over grit-blasted surfaces, one with Al 2024-T3 and another with Al 7075-T6. When wet time was evaluated in the grit-blast designed experiment (2.2.1), data showed that the factor was insignificant for wet times of 10 minutes and 20 minutes, so all times between were also considered to be insignificant. The goal of the wet-time experiments was to define the minimum Boegel-EPII wet time required to provide cohesive failures in the wedge test. Wet times between 2 and 12 minutes at 2-minute intervals were evaluated in this experiment.

Wedge test adherends were treated with grit-blast/sol-gel and primed with BR 6747-1. Wedge test panels were bonded with AF 163-2M adhesive, machined into specimens, measured for bondline thickness, and tested at 140°F and 95-100% RH.

2.2.3.1 Al 20204-T3 Boegel-EPII Wet Time Evaluation

Results of the wet time evaluation on Al 2024-T3 are shown in Table 2.2-3. When varying the wet time between 2 minutes and 12 minutes, there appears to be no difference in either the crack growths or failure modes. Since wet times of 20 minutes were evaluated in the grit-blast designed experiment, there is sufficient data to show that wet times from 2-20 minutes provide acceptable wedge test results on Al 2024-T3 grit-blasted surfaces.

Table 2.2-3: Effect of Boegel Wet Time on Al 2024-T3 Grit-Blast Wedge Test Results

Boegel-EPII Wet Time	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
		1 hr	8 hr	24 hr	7 days	21 days	28 days	
2 minutes	1.18	0.02	0.05	0.07	0.14	0.18	0.20	94% co
4 minutes	1.08	0.06	0.07	0.08	0.18	0.22	0.25	95% co
6 minutes	1.10	0.06	0.08	0.12	0.19	0.22	0.23	95% co
8 minutes	1.09	0.04	0.06	0.08	0.16	0.22	0.22	94% co
10 minutes	1.09	0.04	0.06	0.10	0.16	0.22	0.23	95% co
12 minutes	1.09	0.05	0.07	0.10	0.16	0.23	0.23	95% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.2.3.2 Al 7075-T6 Boegel-EPII Wet Time Evaluation

Results of the wet time evaluation on Al 7075-T6 are shown in Table 2.2-4. As with Al 2024-T3, there appears to be no difference in either crack growths or failure modes of wedge test specimens when the wet time is varied between 2 minutes and 12 minutes. There is sufficient data to show that wet times from 2-20 minutes provide acceptable wedge test results on Al 7075-T6 grit-blasted surfaces since wet times of 20 minutes were evaluated in the grit-blast designed experiment.

Table 2.2-4: Effect of Boegel Wet Time on Al 7075-T6 Grit-Blast Wedge Test Results

Boegel-EPII Wet Time	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
		1 hr	8 hr	24 hr	7 days	21 days	28 days	
2 minutes	1.13	0.08	0.09	0.14	0.21	0.26	0.26	94% co
4 minutes	1.13	0.06	0.07	0.10	0.18	0.23	0.23	96% co
6 minutes	1.16	0.05	0.08	0.09	0.16	0.19	0.20	95% co
8 minutes	1.18	0.06	0.10	0.11	0.20	0.25	0.25	95% co
10 minutes	1.15	0.07	0.10	0.14	0.20	0.24	0.24	94% co
12 minutes	1.21	0.06	0.08	0.08	0.19	0.21	0.22	94% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.2.4 Boegel-EPII Drying Evaluation

2.2.4.1 Dry Method Evaluation

The grit-blast designed experiment (2.2.1) showed that the nitrogen force-dry method for drying Boegel-EPII provided better results in the wedge test than ambient drying at laboratory conditions. An experiment was conducted to determine the effect of force drying Boegel-EPII versus ambient drying for two different wet times, 3 minutes and 10 minutes.

Wedge test adherends were treated with grit-blast/sol-gel, primed with BR 6747-1, and bonded with AF 163-2M adhesive. Panels were machined into specimens, measured for bondline thickness, and tested at 140°F and 95-100% RH. Results are shown in Table 2.2-5. The different dry methods do not appear to affect the wedge test results for either the 3-minute wet time or the 10-minute wet time. Comparable results are obtained using either the ambient dry or force dry.

Table 2.2-5: Effect of Dry Method on Al 2024- T3 Grit-Blast Wedge Test Results

Dry Method	Wet Time	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
			1 hr	8 hr	24 hr	7 days	21 days	28 days	
Ambient dry	3 minutes	1.14	0.01	0.04	0.10	0.14	0.19	0.19	94% co
	10 minutes	1.12	0.01	0.05	0.08	0.17	0.19	0.19	94% co
Nitrogen Force Dry	3 minutes	1.13	0.03	0.07	0.10	0.17	0.22	0.24	95% co
	10 minutes	1.10	0.02	0.08	0.09	0.18	0.21	0.23	93% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.2.4.2 Dry Time Evaluation

The dry time evaluation was conducted in order to generate data for cases where a complete ambient dry of the Boegel-EPII solution (as opposed to force-drying) is desired or required. Two dry times were evaluated in the grit-blast designed experiment (2.2.1), 1 hour and 4 hours. No difference was detected in the designed experiment between the 1 and 4 hour dry times, so the intent of this additional experiment was to determine the minimal dry time required to achieve cohesive failure modes in the wedge test.

Wedge test adherends were treated with grit-blast/sol-gel, primed with BR 6747-1, and bonded with AF 163-2M adhesive. Panels were machined into specimens, measured for bondline thickness, and tested at 140°F and 95-100% RH. Results are shown in Table 2.2-6. The dry time appears to have no effect on the crack growth or failure modes of grit-blasted wedge test specimens. It should be noted that the effect of varying drying temperature and humidity was not evaluated. All drying was conducted at ambient laboratory conditions (70°F and 60% RH).

Table 2.2-6: Effect of Boegel-EPII Dry Time on Al 2024-T3 Grit-Blast Wedge Test Results

Ambient Dry Time	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
		1 hr	8 hr	24 hr	7 days	21 days	28 days	
Force Dry w/N_2	1.17	0.01	0.04	0.07	0.12	0.14	0.16	95% co
15 minutes	1.14	0.02	0.05	0.09	0.14	0.21	0.22	95% co
30 minutes	1.18	0.01	0.06	0.09	0.15	0.21	0.22	96% co
45 minutes	1.13	0.04	0.07	0.09	0.13	0.20	0.20	95% co
60 minutes	1.15	0.01	0.03	0.08	0.12	0.15	0.17	95% co
75 minutes	1.14	0.04	0.07	0.09	0.14	0.19	0.19	94% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.2.5 Primer Evaluation

Adhesive bond primers provide a number of benefits for adhesive joints[10]. The use of bond primers allows treated, unbonded panels to be stored for long periods of time prior to adhesive bonding without repeating the surface preparation. Bond primers may also significantly increase bond environmental durability. Although a need does not exist for storing treated aluminum for long periods prior to repair bonding, the effect of bond primers on bond durability is a concern. This section provides data comparing different primers and varying primer cure cycles.

2.2.5.1 Effect of Primer Type

In the grit-blast designed experiment (section 2.2.1), wedge test specimens primed with Cytec BR 6747-1 were compared to wedge tests specimens fabricated without bond primer. Results of that experiment showed that BR 6747-1 increased the bond durability in the wedge test when compared to specimens without primer. In this experiment, wedge test specimens were fabricated with the following bond primers:

- ***Cytec BR 127:*** solvent-based, chromated bond primer,
- ***Cytec BR 6747-1:*** waterborne, chromated bond primer,

- ***Cytec BR 6757-1****:* experimental waterborne, nonchromated bond primer, and
- ***No bond primer.***

Wedge test adherends were treated with grit-blast/sol-gel, primed with BR 6747-1, and bonded with AF 163-2M adhesive and cured for 60 minutes at 250°F and 35-40 psi in a portable autoclave. Panels were machined into specimens, measured for bondline thickness, and tested at 120°F and 95-100% RH as well as 140°F and 95-100% RH. Results of the wedge tests performed at 120°F and 95-100% RH are shown in Table 2.2-7. Results of the wedge tests performed at 140°F and 95-100% RH are shown in Table 2.2-8.

Table 2.2-7: Effect of Primer on Grit-Blast Wedge Test Results at 120°F and 95-100% RH

Bond Primer	Initial (in)	Cummulative Crack Growth (in)						Failure Mode
		1 hr	8 hr	24 hr	7 days	21 days	28 days	
BR 127	1.16	0.09	0.13	0.15	0.20	0.26	0.29	7% co
BR 6747-1	1.17	0.03	0.05	0.09	0.09	0.15	0.15	97% co
BR 6757-1	1.13	0.05	0.05	0.06	0.10	0.12	0.12	68% co*
No primer	1.09	0.08	0.12	0.15	0.20	0.22	0.23	84% co**

co: cohesive failure within the adhesive layer

* noncohesive failure occurred at the primer-adhesive interface

** noncohesive failure occurred between the aluminum and adhesive

Table 2.2-8: Effect of Primer on Grit-Blast Wedge Test Results at 140°F and 95-100% RH

Bond Primer	Initial (in)	Cummulative Crack Growth (in)						Failure Mode
		1 hr	8 hr	24 hr	7 days	21 days	28 days	
BR 127	1.19	0.08	0.16	0.19	0.27	0.33	0.33	0% co
BR 6747-1	1.06	0.03	0.11	0.11	0.15	0.23	0.24	95% co
BR 6757-1	1.16	0.03	0.07	0.11	0.17	0.17	0.20	83% co*
No primer	1.22	0.07	0.11	0.19	0.26	0.28	0.33	36% co**

co: cohesive failure within the adhesive layer

* noncohesive failure occurred at the primer-adhesive interface

** noncohesive failure occurred between the aluminum and adhesive

When testing at both 120°F and 140°F, only adherends primed with BR 6747-1 exhibit acceptable durability results. Specimens primed with BR 127 exhibited complete interfacial failure between the aluminum and primer. A compatibility problem may exist between the BR 127 bond primer and the Boegel-EPII coating, however the exact cause for failure is unknown at this time. BR 6757-1 exhibits interfacial failure that visually appears to occur between the primer and adhesive. It was difficult to use traditional methods such as Energy Dispersive X-ray Spectrometry (EDX) to determine the exact location of failure due to the fact BR 6757-1 does not contain chromium. In order to identify failure location, EDX is typically used to identify the location of chromium. Chromium is found in the BR 6747-1 bond primer but not the adhesive, so locations where chromium was detected contained primer.

2.2.5.2 Effect of Primer Cure

The requirement for separate primer and adhesive cure cycles can create undesirable time constraints for personnel performing repair adhesive bonding processes. Therefore, the ability to

cocure the primer and adhesive in a single cure cycle was studied. The following three primer cure cycles were evaluated using BR 6747-1 since this primer showed the best performance in the primer type evaluation (section 2.2.5.1):

1. ***Precure (control):*** 30-minute dry at ambient temperature (70°F) then 60 minutes at 250°F per the manufacturer's recommendations prior to bonding,
2. ***Primer Fuse:*** 30-minute dry at ambient temperature followed by heat application via heat gun or oven to "fuse" the primer, then cocure with adhesive for 60 minutes at 250°F, and
3. ***Cocure:*** 30-minute dry at ambient temperature followed by adhesive application and cocure with the adhesive for 60 minutes at 250°F.

BR 6747-1 primer dries as a powdery film when applied. The dried surface appears to be rough and uneven. When cured, the film appears to be uniform and translucent. This same appearance is also achieved by adding heat for a short period of time to flow the primer. This was called "fusing" the primer. For most tests, primer fusing was conducted in an air-circulating oven for 10 minutes at 200°F. Longer times at slightly lower temperatures will also fuse the primer. Fusing the primer allows for easier handling of the panels since the dry powder could be damaged. Fusing does not cure the primer and would not necessarily result in the same performance obtained by completely curing the primer prior to bonding. When "cocuring," adhesive was applied directly to the powdery surface so the primer and adhesive were cured together without first fusing the primer.

Wedge test adherends were treated with grit-blast/sol-gel, primed with BR 6747-1, and bonded with AF 163-2M adhesive. Panels were machined into specimens, measured for bondline thickness, and tested at 140°F and 95-100% RH. Results are shown in Table 2.2-9. All three of the primer cure cycles provided similar crack growths and failure modes after 28 days of aging.

Table 2.2-9: Effect of BR 6747-1 Primer Cure on Grit-Blast Wedge Test Results

Primer Cure Cycle	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
		1 hr	8 hr	24 hr	7 days	21 days	28 days	
Precure	1.06	0.03	0.11	0.11	0.15	0.23	0.24	95% co
Primer fuse	1.06	0.02	0.14	0.14	0.18	0.25	0.28	93% co
Cocure	1.09	0.01	0.14	0.14	0.15	0.24	0.27	95% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.2.5.3 Effect of Cocuring Primer and Adhesive Under Vacuum Pressure

Cocuring the primer and adhesive in a single heat cycle saved processing time and did not appear to present any adverse effects when cured under positive pressure. However, most field-level bonded repairs are performed using vacuum to apply pressure. In order to determine the effect of cocuring the primer and adhesive under vacuum, wedge test panels were fabricated using a grit-blast deoxidation step.

Wedge test adherends were treated with grit-blast/sol-gel, primed with BR 6747-1, and bonded with AF 163-2M adhesive. Adherends for one wedge test panel were precured according to the manufacturer's recommendations and bonded using 35 psi positive pressure during cure. Adherends for another wedge test panel were fabricated using primer cocured with the adhesive under 27 inches Hg vacuum. Both wedge test panels were bonded with AF 163-2M adhesive and cured for 60 minutes at 250°F in a portable autoclave utilizing the different cure pressures. Panels were machined into specimens, measured for bondline thickness, and tested at 120°F and 95-100% RH. Results are shown in Table 2.2-10. There did not appear to be any difference in crack growth or failure mode due to cocuring under vacuum pressure.

Table 2.2-10: Effect of Cocuring Primer and Adhesive Using Vacuum Pressure on Grit-Blast Wedge Test Results

Primer Cure Cycle	Adhesive Cure Pressure	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
			1 hr	8 hr	24 hr	7 days	21 days	28 days	
Precure	35 psi	1.17	0.03	0.05	0.05	0.09	0.15	0.15	97% co
Cocure	27 in Hg	1.12	0.04	0.05	0.06	0.10	0.13	0.14	98% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.2.5.4 Effect of Primer Application Method

Field-level and depot maintenance personnel have expressed interest in the ability to apply bond primers without the use of a spray gun. It is easier to apply primer with a brush or cloth versus applying primer with a spray gun, and health and safety concerns are increased when hazardous materials such as chromium are atomized in the air, especially in poorly ventilated areas. For these reasons, an experiment was conducted to determine the effect of applying primer with a lint-free cloth versus spray-application.

Two wedge test panels per condition were fabricated for this experiment. Wedge test adherends were treated with grit-blast/sol-gel, primed with BR 6747-1, and bonded with AF 163-2M adhesive. Panels were machined into specimens, measured for bondline thickness, and tested at 120°F and 95-100% RH. Results are shown in Table 2.2-11. Although there was little difference in amount of crack growth due to the primer application method, there was a difference in failure mode. The specimens primed with a lint-free cloth exhibited lower percentages of cohesive failure than the panels primed with the spray gun.

Table 2.2-11: Effect of Primer Application Method on Grit-Blast Wedge Test Results

Primer Application Method	Initial (in)	Cummulative Crack Growth (in)							Failure Mode*
		1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
Binks 105 spray gun	1.16	0.04	0.07	0.07	0.14	0.15	0.16	0.18	98% co
	1.10	0.04	0.05	0.08	0.11	0.13	0.14	0.17	97% co
Lint-free cloth	1.05	0.07	0.07	0.11	0.15	0.17	0.17	0.20	91% co
	1.19	0.05	0.07	0.11	0.15	0.17	0.18	0.19	91% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.2.6 Effect of Epoxy Film Adhesive

Although 3M Company AF 163-2M adhesive was chosen for use in optimizing the sol-gel surface preparations, a number of other 250°F-curing epoxy-film adhesives are used for field and depot-level bonded repair. Therefore, wedge test panels were bonded with 3M Company AF 163-2M (control), Cytec FM 73M, Loctite Hysol EA 9628, and Loctite Hysol EA 9696 adhesives to determine the effect of different film adhesives. Each adhesive was 0.06psf weight and was manufactured with a mat carrier.

Al 7075-T6 wedge test adherends were treated with grit-blast/sol-gel, primed with BR 6747-1, and bonded with adhesive. Panels were machined into specimens, measured for bondline thickness and tested at 140°F & 95-100% RH. Results are shown in Table 2.2-12. AF 163-2M specimens exhibited the largest crack growth and largest nicks of adhesional failure at the edges of the specimens after 28 days in humidity. Specimens bonded with FM 73M, EA 9628, and EA 9696 exhibited cohesive failure modes. Cytec FM 73M, Loctite Hysol EA 9628 and Loctite Hysol EA 9696 all appear to yield acceptable wedge test results when used with the grit-blast deoxidation step and Boegel-EPII solution.

Table 2.2-12: Effect of Adhesive Type on Grit-Blast Wedge Test Results

Adhesive	Initial (in)	Cummulative Crack Growth (in)					Failure Mode*
		1 hr	8 hr	24 hr	7 days	28 days	
3M Company AF 163-2M	1.15	0.05	0.08	0.13	0.18	0.26	94% co
Cytec Fiberite FM 73M	1.26	0.00	0.01	0.01	0.06	0.12	96% co
Loctite Hysol EA 9628	1.36	0.00	0.00	0.03	0.08	0.16	100% co
Loctite Hysol EA 9696	1.29	0.02	0.04	0.05	0.12	0.17	100% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.2.7 Initial Bond Strength Results

In order to determine the initial strengths of bonded joints using Boegel-EPII over a grit-blasted surface, tensile lap shear[11] and floating roller peel[12] tests were conducted. This was to ensure the initial strength of grit-blasted bonded joints treated with Boegel-EPII, without the effect of moisture conditioning, is similar to that of PAA-prepared bonded joints.

Al 2024-T3 adherends were treated with grit-blast/sol-gel. BR 6747-1 was used for the primed specimens and was dried at ambient temperature (70°F) for 30 minutes. Primer on some specimens was precured according to the manufacturer's recommendations while on others it was cocured with the adhesive (without fusing). All panels were bonded with AF 163-2M adhesive and cured for 60 minutes at 250°F and 35-40 psi in a portable autoclave. Lap shear testing was performed at –65°F, 70°F, and 180°F after a four-minute soak at temperature. Floating roller peel testing was performed at 70°F and –65°F after a four-minute soak at temperature. Published data from 3M Company[13] on AF 163-2M using chromic acid anodize (CAA) primed with EC-3917 (solvent-based, chromated, bond primer) as well as PAA control panels primed with BR 6747-1 and cured according to the manufacturer's recommendations were used to compare initial strength results. Lap shear results are shown in Table 2.2-13.

Floating roller peel test results are shown in Table 2.2-14. All data points are the average of five specimens from a single panel.

Table 2.2-13: Tensile Lap Shear Test Results for Grit-Blasted Al 2024-T3

Surface Prep	Primer	Lap Shear Strength (psi) [% Cohesive Failure]		
		-65°F	70°F	180°F
grit-blast sol-gel	BR 6747-1 [p]*	5778 [68%]	5796 [100%]	3770 [22%]
grit-blast sol-gel	BR 6747-1 [c]**	5946 [84%]	5382 [100%]	3644.1 [77%]
grit-blast sol-gel	none	6038 [91%]	5430 [98%]	3773 [22%]
PAA	BR 6747-1 [p]	6398 [56%]	6028 [100%]	4159 [28%]
Published data on CAA Al 2024-T3	EC-3917	6400	5700	3600

* [p]: primer precured according to manufacturer's recommendations

** [c]: primer cocured with adhesive

Table 2.2-14: Floating Roller Peel Test Results for Grit-Blasted Al 2024-T3

Surface Prep	Primer	Peel Strength (pli) [% cohesive]	
		-65°F	70°F
grit-blast sol-gel	BR 6747-1 [p]*	51.1 [43%]	76.6 [100%]
grit-blast sol-gel	BR 6747-1 [c]**	64.3 [79%]	68.8 [100%]
PAA	BR 6747-1 [p]*	62.2 [90%]	72.7 [100%]
Published data on FPL etched Al 2024-T3	EC-3924B	58.0	79.0

* [p]: primer precured according to manufacturer's recommendations

** [c]: primer cocured with adhesive

2.3 Optimization of Processing Parameters Using Boegel-EPII with Nylon-pad Abrasion Surface Activation Techniques

As anticipated, the use of grit-blasting (Section 2.2) with Boegel-EPII solution can produce an excellent surface for adhesive bonding with good initial strength and bond durability results. However, one goal of this project was to eliminate grit-blasting since it can be difficult to properly perform, particularly on aircraft. Containment and clean-up efforts represent a significant inconvenience and increased repair time, especially for bonding applications in sensitive areas of the aircraft such as inside wing fuel tanks. Airborne grit can also be a health/safety concern.

The use of nylon pads to abrade the surface prior to application of the Boegel-EPII solution would be a simple replacement for the grit-blasting step. It was anticipated that the more reactive Boegel-EPII chemistry might yield acceptable moisture durability results as measured by the wedge test, whereas this approach was not successful for the silane surface preparation[8]. Abrasion could be accomplished using an air-driven rotary tool that is available in most field-level maintenance facilities. However, a potential drawback to nylon-pad abrasion is the increased difficulty in visually detecting organic contamination on the abraded surface as compared to a grit-blasted surface. In addition, it is more difficult to consistently achieve and verify a properly abraded surface.

In order to optimize the process parameters involved with activating the bonding surface and subsequent application of Boegel-EPII and bond primers, a designed experiment was conducted to determine significant processing factors. Once identified, several smaller experiments were conducted to determine optimum operating windows for individual steps in the surface preparation.

2.3.1 Nylon-pad Abrasion Designed Experiment

In order to evaluate several key processing factors using a nylon-pad abraded deoxidation process with Boegel-EPII solution, a designed experiment was conducted using an L16 array. The evaluated processing factors are listed in Table 2.3-1. Aluminum alloy type, grind time, time between deoxidation and application of Boegel-EPII solution (post-abrade time), Boegel-EPII wet time, Boegel-EPII dry method, Boegel-EPII dry time, and bond primer cure cycle factors were all evaluated using a matrix consisting of 16 wedge test panels.

Table 2.3-1: Nylon-pad Deoxidation Designed Experiment Processing Parameters

Factor	Parameter #1	Parameter #2
Alloy	Al 2024-T3	Al 7075-T6
Grind time	1 minute	2 minutes
Post-abrade time	<1 minute	30 minutes
Boegel-EPII wet time	3 minutes	10 minutes
Dry method	nitrogen force	ambient dry
Dry time	30 minutes	60 minutes
Primer cure	Precure	Cocure

Wedge test adherends were cleaned with acetone and wiped with lint-free wipes until no remaining trace of grease, dirt, or contamination was visibly present. The panels were then abraded with general purpose Scotch-Brite™ pads (3M Company) until a polished surface was obtained, with the abrasion debris removed by wiping with lint-free wipes moistened with acetone. This initial nylon-pad abrasion step was used to generate a baseline surface to start the process. All panels were then abraded with 3-inch diameter Standard Abrasive fine “Buff and Blend” pads on a 20,000rpm high-speed grinder for the specified grind time. Clean, dry compressed nitrogen was used to drive the high-speed grinder in order to prevent contamination from oil, condensed moisture, or other contaminants. After the panels were abraded, 40 psi compressed nitrogen was used to remove as much residue from the surface as possible, without the use of solvents. At this point, panels were allowed to sit for a specified time (post-abrade time) at ambient conditions (70°F and 60% relative humidity) to determine if a maximum acceptable time existed between deoxidation and Boegel-EPII solution application. Boegel-EPII solution was applied via brush within 1 minute or after 30 minutes of abrasion, and the surface was kept wet for the specified time. The panels were ambient dried or force-dried using 40 psi nitrogen. Once dry, panels were primed with BR 6747-1 primer to a thickness of 0.1-0.3 mil. Primed panels were dried at ambient conditions for 30 minutes prior to cure. After drying, the primer cure was accomplished in one of two ways: (1) precuring at 250°F for 60 minutes per manufacturer’s directions or (2) “fusing” the primer using a heat gun followed by cocuring with AF 163-2M adhesive for 60 minutes at 250°F.

Panels were machined into 1.0-inch wide specimens, and the bondline of each specimen was measured with an optical microscope. The specimens were then tested at 120°F and 95-100% RH. The crack growths of the specimens after 28 days were used to calculate the significance of each factor using the design of experiments philosophy. Figure 2.3-1 shows the calculated significance of each factor to the 95% confidence limit. All factors or interactions having a standardized effect greater than the 95% confidence limit were considered significant.

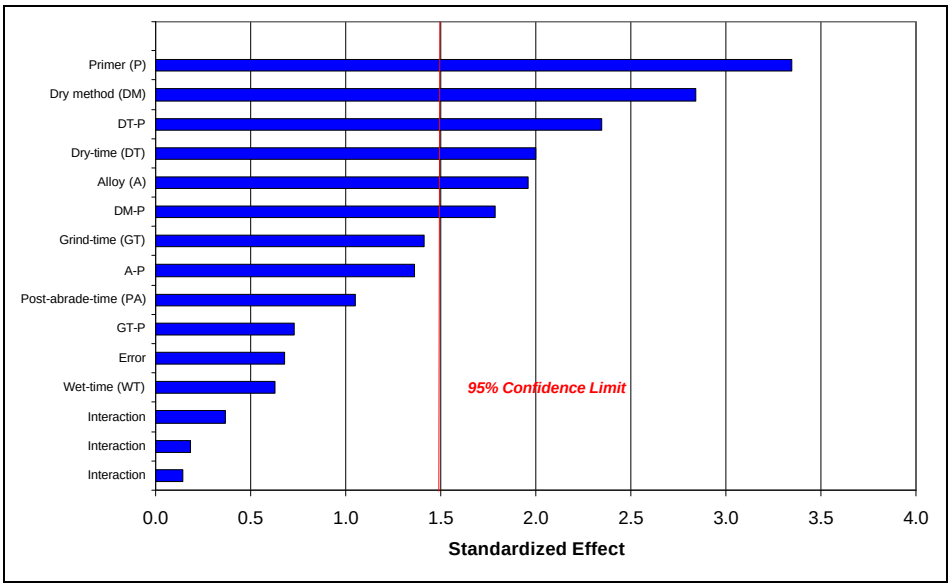


Figure 2.3-1: Significance of Nylon-Pad Deoxidation Processing Factors

The wet time and post-abrade time factors, along with a few interactions, were considered insignificant. The optimum set of processing factors for the nylon-pad/sol-gel surface preparation is listed in Table 2.3-2. The two most significant factors are dry method and primer cure method. Panels that were ambient dried and cocured with the adhesive performed the best.

Table 2.3-2: Optimum Processing Parameters for Nylon-Pad Deoxidation Process

Factor	**Optimum Parameter**
Alloy	Al 2024-T3
Grind time	2 minutes
Dry method	ambient dry
Dry time	30 minutes
Primer cure	Cocure
*Post-abrade time**	*<1 minute*
*Boegel-EPII wet time**	*10 minutes*

* insignificant

Since there were no panels fabricated with the complete set of "optimal" processing parameters as determined by the designed experiment, a separate test was conducted to validate the experiment. Al 2024-T3 wedge test specimens were fabricated with AF 163-2M utilizing the

designed experiment optimum nylon-pad process from Table 2.3-2. The specimens were tested at 120°F and 95-100% RH as well as 140°F and 95-100% RH. Results are shown in Table 2.3-3. Cohesive failure modes were witnessed after 28 days at 120°F and 95-100% RH (Figure 2.3-2). However, a small amount of adhesional failure occurred at the edges and toward the center of the AF 163-2M specimens that were tested at 140°F and 95-100% RH (Figure 2.3-3). The verification panels validated the designed experiment since all specimens tested at 120°F failed cohesively after 28 days of exposure.

Table 2.3-3: Nylon Pad Designed Experiment Verification

Testing Conditions	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
		1 hr	8 hr	24 hr	7 days	21 days	28 days	
120°F & 95-100% RH	1.13	0.00	0.08	0.12	0.13	0.13	0.14	96%co
140°F & 95-100% RH	1.19	0.04	0.09	0.09	0.19	0.26	0.27	91% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

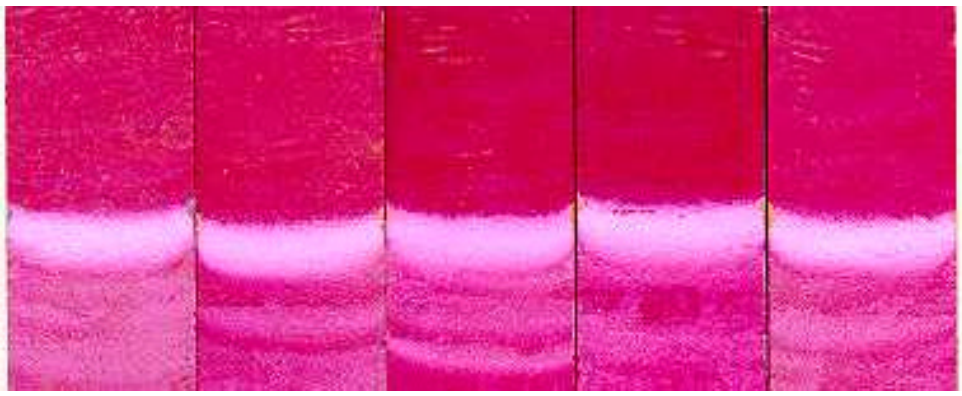


Figure 2.3-2: Failure Mode Exhibited by "Optimal" Nylon-Pad Deoxidized Specimens Treated with Boegel-EPII and Tested at 120°F and 95-100% Relative Humidity

Figure 2.3-3: Failure Mode Exhibited by "Optimal" Nylon-Pad Deoxidized Specimens Treated with Boegel-EPII and Tested at 140°F and 95-100% Relative Humidity

2.3.2 Effect of Solvent Type on Nylon-pad Deoxidation Process

Environmental regulations vary from location to location. Numerous locales have tight regulations restricting the use of volatile solvents such as methylethyl ketone (MEK). Due to the variability of these restrictions, several different solvents are used depending on the restrictions in place. Therefore, wedge test panels were fabricated using various solvents for degreasing in order to determine if the solvent caused differences in bond durability. Three different solvents were used in this investigation: acetone, MEK, and isopropyl alcohol (IPA).

Al 2024-T3 wedge test adherends were cleaned using different solvents, treated with the nylon-pad/sol-gel process (2.3.1), primed with BR 6747-1 and bonded with AF 163-2M adhesive. Primer and adhesive were cocured. Wedge test panels were machined into specimens, measured for bondline thickness, and tested at 120°F & 95-100% RH. Results are shown in Table 2.3-4. There appeared to be no difference in either crack growth or failure mode due to solvent type. However, it should be noted that the adherends used in this program were fairly clean to prior to processing as compared to typical aircraft structure that may be contaminated with dirty water, oil, fuel, hydraulic fluid, and more. Therefore, the full effect of using different solvents for degreasing, especially in a field-level environment, was not accurately depicted in this experiment.

Table 2.3-4: Effect of Solvent Type on Nylon Pad Wedge Test Results

Solvent	Initial (in)	Cummulative Crack Growth (in)							Failure Mode*
		1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
Isopropyl alcohol	1.11	0.04	0.07	0.09	0.13	0.15	0.17	0.18	96%co
Acetone	1.19	0.04	0.07	0.09	0.13	0.15	0.17	0.17	96%co
MEK	1.13	0.06	0.09	0.11	0.16	0.18	0.18	0.20	96% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.3.3 Effect of Nylon Pad Manufacturer

Several types of nylon pads are currently manufactured, sold, and used commercially. 3M Company and Standard Abrasives are among the current manufacturers. In order to determine the variability in the performance of the nylon pad due to manufacturer and pad grade (coarseness), an experiment was conducted using different types and grades of nylon pads for deoxidation prior to application of Boegel-EPII solution.

Al 2024-T3 wedge test adherends were treated with the nylon-pad/sol-gel process, primed with BR 6747-1, and bonded with AF 163-2M adhesive. Primer and adhesive were cocured. Wedge test panels were machined into specimens, measured for bondline thickness, and tested at 120°F & 95-100% RH. Results are shown in Table 2.3-5. Overall, panels abraded with the 3M Company pads appear to yield smaller crack growths and higher percentages of cohesive failure than the Standard Abrasives pads. The 3M medium and coarse pads and Standard Abrasive medium pads provided the best overall results in the wedge test.

Table 2.3-5: Effect of Nylon Pad Grade and Manufacturer on Nylon Pad Wedge Test Results

Nylon Pad	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
		1 hr	8 hr	24 hr	7 days	21 days	28 days	
3M Very Fine	1.08	0.02	0.09	0.10	0.12	0.16	0.16	95% co
3M Medium	1.14	0.00	0.04	0.05	0.07	0.10	0.10	97% co
3M Coarse	1.09	0.02	0.07	0.08	0.09	0.11	0.12	98% co
SA Fine	1.07	0.04	0.09	0.10	0.15	0.19	0.19	94% co
SA Medium	1.09	0.02	0.09	0.10	0.13	0.15	0.15	97% co
SA Coarse	1.11	0.03	0.13	0.13	0.15	0.19	0.21	94% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.3.4 Effect of Abrasion Time

Quantifying a properly abraded surface for adhesive bonding is important for quality control. This is particularly difficult for a nylon-pad-abraded surface where the process of abrading is heavily dependent on the technician performing the operation. In an attempt to determine the minimal amount of abrading required to effectively deoxidize an aluminum surface for adhesive bonding, several wedge test panels were fabricated while varying the amount of time used to abrade the bond surfaces. The evaluated abrading times (30 to 120 seconds) were practical for a 6.5 inch by 6.5 inch wedge adherend. Less than 30 seconds abrasion for a 6.5-inch by 6.5-inch area would not have been enough time to abrade the entire panel. More than 120 seconds per 6.5-inch by 6.5-inch area was considered impractical for large parts in a field environment due to time limitations.

Al 2024-T3 wedge test adherends were treated with the nylon-pad/sol-gel process using different abrasion times, primed with BR 6747-1 and bonded with AF 163-2M adhesive. Wedge test panels were machined into specimens, measured for bondline thickness, and tested at 120°F & 95-100% RH. Results are shown in Table 2.3-6. There does not appear to be a correlation between abrasion time and wedge test results since all specimens failed cohesively with very similar crack growths.

Table 2.3-6: Effect of Abrasion Time on Nylon Pad Wedge Test Results

Abrasion Time	Initial (in)	Cummulative Crack Growth (in)							Failure Mode*
		1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
30 seconds	1.12	0.01	0.03	0.05	0.14	0.15	0.16	0.16	95% co
60 seconds	1.12	0.04	0.06	0.07	0.11	0.12	0.15	0.15	96% co
90 seconds	1.16	0.03	0.04	0.08	0.12	0.13	0.15	0.15	96% co
120 seconds	1.14	0.01	0.04	0.06	0.11	0.14	0.14	0.14	96% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.3.5 Effect of Time Between Deoxidation and Application of Boegel-EPII Solution

During the nylon pad designed experiment (2.3.1), the time between deoxidation and application of Boegel-EPII solution (post-abrade time) was evaluated and determined to be insignificant between one and thirty minutes. In order to further evaluate this processing factor and define the operating window, a follow-on experiment was conducted to determine the effect of increased time between deoxidation using the nylon-pad/sol-gel process.

Al 2024-T3 wedge test adherends were treated with the nylon-pad/sol-gel process varying the time between abrasion and application of sol-gel. Panels were primed with BR 6747-1 and bonded with AF 163-2M adhesive. Wedge test panels were machined into specimens, measured for bondline thickness, and tested at 120°F & 95-100% RH. Results are shown in Table 2.3-7. Although the failure mode is less desirable for the 30-minute wait prior to application of Boegel-EPII solution, it does not appear that a drastic change in wedge test performance was detected due to time between deoxidation and application of Boegel-EPII solution. From the results of the designed experiment and this experiment, it appears the time between the deoxidation step and application of Boegel-EPII solution is insignificant for times between 1 and 120 minutes, under laboratory conditions.

Table 2.3-7: Effect of Increased Time Between Deoxidation Using Nylon Pads and Application of Boegel-EPII Solution

Post-Deoxidation Time	Initial (in)	Cummulative Crack Growth (in)							Failure Mode*
		1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
within 1 minute	1.17	0.02	0.07	0.08	0.16	0.18	0.18	0.20	95% co
30 minutes	1.16	0.06	0.11	0.12	0.17	0.19	0.21	0.22	89% co
90 minutes	1.16	0.06	0.11	0.12	0.17	0.19	0.21	0.22	95% co
120 minutes	1.11	0.00	0.08	0.08	0.10	0.13	0.15	0.15	98% co

* co: cohesive failure within adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.3.6 Boegel-EPII Wet Time Evaluation

During the nylon pad designed experiment (section 2.3.1), the effect of varying the wet time of Boegel-EPII solution on an abraded surface was evaluated for 3 minutes and 10 minutes. Although the wet time processing factor was found to be insignificant to the 95% confidence level, additional data was desired. Therefore, an experiment was conducted to determine the effect of varying wet time between 2 and 20 minutes.

Al 2024-T3 wedge test adherends were treated with the nylon-pad/sol-gel process varying the sol-gel wet time. Panels were primed with BR 6747-1 and bonded with AF 163-2M adhesive. Wedge test panels were machined into specimens, measured for bondline thickness, and tested at 120°F & 95-100% RH. Results are shown in Table 2.3-8. Wetting the nylon-pad-abraded surface for times between 2 minutes and 20 minutes appeared to have no effect on wedge test results.

Table 2.3-8: Effect of Boegel-EPII Wet Time on Nylon Pad Wedge Test Results

Wet Time	Initial	Cummulative Crack Growth (in)							Failure
	(in)	1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	Mode*
2 minutes	1.17	0.07	0.11	0.11	0.16	0.18	0.18	0.18	99% co
4 minutes	1.13	0.08	0.13	0.13	0.17	0.18	0.20	0.24	97% co
6 minutes	1.12	0.08	0.10	0.10	0.16	0.18	0.18	0.20	99% co
8 minutes	1.15	0.03	0.10	0.11	0.17	0.18	0.18	0.19	99% co
10 minutes	1.14	0.06	0.08	0.09	0.12	0.15	0.18	0.18	99% co
12 minutes	1.13	0.04	0.07	0.08	0.12	0.13	0.14	0.16	99% co
20 minutes	1.13	0.05	0.10	0.11	0.15	0.17	0.18	0.19	98% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.3.7 Effect of Boegel-EPII Dry Method

Upon completion of the Boegel-EPII wet time, the bonding surface must be dried before application of bond primer or adhesive. Two methods were evaluated during the nylon pad designed experiment (section 2.3.1): force dry with 40 psi compressed nitrogen and 30-minute ambient-temperature dry in a controlled laboratory environment. The designed experiment showed that panels dried vertically for 30 minutes at ambient temperature exhibited better results than panels blown dry with 40 psi compressed nitrogen. However, when performing surface preparations in the field or at depot level, maintenance personnel do not want to wait 30 minutes to begin the next processing step, and there is also a danger of contaminating the bonding surface during this 30-minute drying period. In addition, the surfaces to be treated may exist at an orientation other than vertical, and may possess geometry that allows the sol-gel solution to puddle and not readily dry in 30 minutes and/or result in excessively thick sol-gel film. Therefore, force drying with nitrogen or clean, dry air would be more practical. In order to determine the effect of Boegel-EPII solution drying method, an experiment was conducted varying the drying method (ambient and force-dry), ambient dry time (10 minutes and 30 minutes), and nitrogen line pressure (5 to 50 psi).

Al 2024-T3 wedge test adherends were treated with the nylon-pad/sol-gel process varying the sol-gel drying time. Adherends were dried either at ambient laboratory temperature or force dried with compressed nitrogen. Various dry times and nitrogen pressures were used to dry the adherends. Once dried, panels were primed with BR 6747-1 and bonded with AF 163-2M adhesive. Wedge test panels were machined into specimens, measured for bondline thickness, and tested at 120°F & 95-100% RH. Results are shown in Table 2.3-9.

When ambient drying in a controlled laboratory environment, there appears to be no difference between drying for 30 minutes or 10 minutes prior to application of the primer. However, drying times in the field or depot will likely be different due to the actual temperature and humidity experienced while performing the surface preparation. When force drying the panels using compressed nitrogen, good failure modes are noticed up to pressures of 40 psi with a standoff distance of 6-8 inches. A loss in percentage of cohesive failure mode is noticed when drying panels with 50 psi nitrogen. Panels dried with 5-20 psi nitrogen exhibited crack growth and failure modes similar to those of panels dried at ambient laboratory conditions for 30 minutes.

Standoff distance was not evaluated as a parameter of drying in this experiment although it could be a significant factor. This could be especially true if the stand off distance were too short, causing higher pressures on the bond surfaces.

Table 2.3-9: Effect of Drying Method on Nylon Pad Wedge Test Results

Dry Method	Initial (in)	Cummulative Crack Growth (in)							Failure Mode*
		1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
30 min @ RT	1.10	0.05	0.09	0.13	0.16	0.17	0.20	0.21	98% co
10 min @ RT	1.12	0.02	0.08	0.11	0.18	0.20	0.20	0.23	97% co
N_2 force dry (5 psi)	1.11	0.01	0.01	0.03	0.10	0.12	0.14	0.18	99% co
N_2 force dry (10 psi)	1.12	0.02	0.03	0.05	0.11	0.13	0.15	0.20	98% co
N_2 force dry (20 psi)	1.15	0.00	0.05	0.08	0.15	0.16	0.17	0.22	99% co
N_2 force dry (30 psi)	1.20	0.02	0.05	0.10	0.14	0.15	0.17	0.22	94% co
N_2 force dry (40 psi)	1.10	0.03	0.05	0.08	0.13	0.15	0.15	0.20	99% co
N_2 force dry (50 psi)	1.21	0.07	0.11	0.13	0.19	0.23	0.26	0.31	80% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.3.8 Effect of Primer Application Method

Although spray application of bond primer in a laboratory setting is convenient, priming in field-level and depot environments with spray guns is often difficult due to equipment limitations and safety regulations concerning hazardous airborne materials. Therefore, maintenance personnel would like the option of applying bond primer using a manual-wipe method. This could include brushing, rolling, or wiping with some type of cloth. For this evaluation, wiping the primer with a lint-free wipes (Duralace® 9404 from Chicopee®) was compared to applying the primer with a spray gun, analogous to the evaluation conducted for grit-blast/sol-gel (section 2.2.5.4).

Al 2024-T3 wedge test adherends were treated with the nylon-pad/sol-gel process and primed with BR 6747-1, varying the application method. Panels were then bonded with AF 163-2M adhesive. Wedge test panels were machined into specimens, measured for bondline thickness, and tested at 120°F & 95-100% RH. Two wedge test panels (a total of 10 specimens) were fabricated for each condition. Results are shown in Table 2.3-10. Using a spray gun to apply the primer resulted in consistent cohesive failure modes. However, using a lint-free cloth to apply the primer resulted in one panel resulting in roughly 97% cohesive failure and the other with 93% cohesive failure. It should be noted that no effort was made to optimize the nonspray application technique. This will be undertaken in a future effort.

2.3.9 Primer Cure Evaluation

The effect of altering the cure cycle for BR 6747-1 primer from the manufacturer's recommended cure (precure) was evaluated using a grit-blast activation step in section 2.2.5.2. Primer fuse and cocure processes were two alternate cure cycles evaluated to decrease the amount of time required to perform a bonded repair and eliminate the for heat lamps typically used to precure primer on aircraft. Precure and cocure processes were evaluated using the nylon-pad activation step in the nylon pad designed experiment (2.3.1). However, more data was

desired to establish the baseline properties when curing the primer under different conditions. Three primer cure cycles were evaluated using BR 6747-1:

1. ***Precure (control):*** 30-minute dry at ambient temperature (70°F) and 60 minutes at 250°F per the manufacturer's recommendations prior to bonding,
2. ***Primer Fuse:*** 30-minute dry at ambient temperature followed by heat application via heat gun or oven to "fuse" primer, then cocure with adhesive for 60 minutes at 250°F, and
3. ***Cocure:*** 30-minute dry at ambient temperature followed by adhesive application and cure per the manufacturer's instructions.

Al 2024-T3 wedge test adherends were treated with the nylon-pad/sol-gel process. Panels were primed with BR 6747-1, varying the cure method, and bonded with AF 163-2M adhesive. Wedge test panels were machined into specimens, measured for bondline thickness, and tested at 120°F & 95-100% RH. Results are shown in Table 2.3-11. A small reduction in the amount of cohesive failure was detected in the "primer fuse" specimens.

Table 2.3-10: Effect of Primer Application Method on Nylon Pad Wedge Test Results

Primer Application Method	Initial (in)	Cummulative Crack Growth (in)							Failure Mode*
		1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
Spray Gun Application	1.10	0.07	0.10	0.11	0.18	0.18	0.21	0.23	97% co
	1.14	0.03	0.08	0.08	0.01	0.16	0.19	0.19	98% co
Wipe Application Using Lint-Free Cloth	1.12	0.09	0.11	0.13	0.15	0.17	0.19	0.20	93% co
	1.17	0.07	0.07	0.11	0.13	0.15	0.17	0.18	97% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

Table 2.3-11: Effect of Primer Cure on Nylon Pad Wedge Test Results

Primer Cure Cycle	Initial (in)	Cummulative Crack Growth (in)							Failure Mode*
		1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
Precure	1.11	0.08	0.10	0.12	0.14	0.18	0.19	0.19	96% co
Primer fuse	1.10	0.06	0.10	0.11	0.17	0.20	0.23	0.23	91% co
Cocure	1.14	0.09	0.11	0.15	0.18	0.19	0.20	0.20	98% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.3.10 Effect of Aluminum Alloy

Several different aluminum alloys are used for the manufacture of aircraft components. Since adhesive bonds will be used for a variety of alloys, mostly 2000 or 7000 series, an experiment was conducted to determine the effect of bonding to either Al 2024-T3 or Al 7075-T6, analogous to the evaluation conducted for grit-blast/sol-gel (section 2.2.2).

Wedge test adherends were treated with the nylon-pad/sol-gel process varying the alloy. Panels were primed with BR 6747-1 and bonded with AF 163-2M adhesive. Wedge test panels were machined into specimens, measured for bondline thickness, and tested at 120°F & 95-100% RH.

Results are shown in Table 2.3-12. There appears to be no difference in the failure mode or crack growths due to aluminum alloys tested.

Table 2.3-12: Effect of Aluminum Alloy on Nylon Pad Wedge Test Results

Aluminum Alloy	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
		1 hr	8 hr	24 hr	7 days	21 days	28 days	
Al 2024-T3	1.06	0.02	0.07	0.10	0.10	0.15	0.15	94% co
Al 7075-T6	1.16	0.02	0.04	0.07	0.09	0.15	0.15	95% co

* co: cohesive failure within the adheive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.3.11 Effect of Cure Cycle Pressure Application Technique

In order to achieve the best mechanical properties from an adhesive, it must typically be processed under positive pressure in an autoclave. However, when performing a bonded repair at the depot or in the field, particularly on aircraft, applying positive pressure may be difficult or impossible. Therefore, it is common practice to use a vacuum bag to apply pressure to a bonded repair. However, this approach can increase porosity content and lead to weaker bond strength[14]. Therefore, wedge tests were conducted in order to determine the effect of cure pressure on bond durability. Tensile lap shear and floating roller peel tests were conducted using vacuum cure cycles to evaluate the effect on strength. Those data can be found in section 2.3.14.

Al 2024-T3 wedge test adherends were treated with the nylon-pad/sol-gel process. Panels were primed with BR 6747-1 and bonded with AF 163-2M adhesive. Panels were cured using 35-40 psi positive pressure, 15 inches Hg vacuum pressure, or full vacuum pressure (27 inches Hg). Wedge test panels were machined into specimens, measured for bondline thickness, and tested at 120°F & 95-100% RH. Results are shown in Table 2.3-13. Although the vacuum-cured specimens exhibited shorter crack growths, the failure modes of the positive pressure and vacuum specimens were all cohesive. Therefore, it did not appear as if vacuum curing altered the durability of the adhesive bond.

Table 2.3-13: Effect of Cure Pressure on Nylon Pad Wedge Test Results

Cure Pressure	Initial (in)	Cummulative Crack Growth (in)							Failure Mode*
		1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
27 inches Hg	1.12	0.04	0.05	0.06	0.10	0.13	0.13	0.14	98% co
15 inches Hg	1.20	0.04	0.08	0.10	0.14	0.17	0.17	0.17	98% co
35-40 psi	1.10	0.05	0.09	0.13	0.16	0.17	0.20	0.21	98% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.3.12 Effect of Epoxy Film Adhesive

Although 3M Company AF 163-2M adhesive was chosen for use in optimizing the sol-gel surface preparations, a number of other 250°F-curing epoxy-film adhesives are used for field and depot-level bonded repair. Therefore wedge test panels were bonded with 3M Company AF

163-2M (control), Cytec FM 73, and Hysol EA 9628 adhesives to determine the effect of different film adhesives. Each adhesive was 0.06psf weight. AF 163-2M and EA 9628 and was manufactured with a mat carrier while FM 73 was manufactured with a knit carrier. Testing in this section is analogous to the evaluation conducted for grit-blast/sol-gel (section 2.2.6).

Al 2024-T3 wedge test adherends were treated with the nylon-pad/sol-gel process. Panels were primed with BR 6747-1 and bonded with adhesive. Panels were machined into specimens, measured for bondline thickness, and tested at both 120°F & 95-100% RH and 140°F & 95-100% RH. Results of the specimens tested at 120°F & 95-100% RH are shown in Table 2.3-14. Results of the specimens tested at 140°F & 95-100% RH are shown in Table 2.3-15.

When tested at 120°F and 95-100% RH, specimens bonded with the three adhesives exhibit good crack growth and failure modes. However, when tested at 140°F and 95-100% RH, only specimens bonded with EA 9628 exhibit failure modes in excess of 95% cohesive. Similar specimens bonded with AF 163-2M and FM 73 exhibited lower percentages of cohesive failure.

Table 2.3-14: Effect of Film Adhesive on Nylon Pad Wedge Test Results when Tested at 120°F and 95-100% RH

Adhesive	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
		1 hr	8 hr	24 hr	7 days	21 days	28 days	
AF 163-2M	1.07	0.02	0.08	0.12	0.16	0.16	0.20	96% co
EA 9628	1.35	0.02	0.08	0.08	0.12	0.12	0.12	97% co
FM 73	1.06	0.00	0.02	0.05	0.07	0.08	0.08	94% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

Table 2.3-15: Effect of Film Adhesive on Nylon Pad Wedge Test Results when Tested at 140°F and 95-100% RH

Adhesive	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
		1 hr	8 hr	24 hr	7 days	21 days	28 days	
AF 163-2M	1.08	0.06	0.10	0.13	0.21	0.24	0.25	90% co
EA 9628	1.37	0.02	0.06	0.09	0.16	0.21	0.22	96% co
FM 73	1.00	0.05	0.10	0.12	0.20	0.23	0.25	90% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

Although the FM 73 (0.06psf) data appeared to be comparable to AF 163-2M data (Table 2.3-14 and Table 2.3-15), further work was conducted after personnel from WR-ALC/TIEDD (Robins AFB, GA) were unable to reproduce similar results using the same process with 0.085psf FM 73 adhesive. Wedge test panels were fabricated using Al 2024-T3 adherends and the same surface preparation utilized in the previous adhesive evaluation, however, the effect of precuring the BR 6747-1 primer was also evaluated. When required, primer was precured as described in section 2.3.9. Panels were bonded with FM 73 (0.085psf) knit carrier adhesive and AF 163-2M (0.06psf) mat carrier adhesive for 60 minutes at 250°F and 35-40 psi in a portable autoclave. Panels were machined into specimens, measured for bondline thickness, and tested at 120°F & 95-100% RH. Results are shown in Table 2.3-16. Cocured FM 73 wedge test specimens exhibited a larger amount of adhesional failure when compared to cocured AF 163-2M

specimens. These results have been repeated in follow-on testing by both AFRL/MLSA and WR-ALC/TIEDD. The reason for the results is unknown at this time.

Table 2.3-16: Additional FM 73 Wedge Test Data at 120°F and 95-100% RH

Primer Cure	Adhesive	Initial (in)	Cummulative Crack Growth (in)							Failure Mode
			1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
Cocure	AF 163-2M	1.05	0.07	0.10	0.14	0.18	0.18	0.20	0.20	99% co
	FM 73	1.03	0.07	0.12	0.14	0.15	0.17	0.21	0.22	87% co
Precure	AF 163-2M	1.07	0.01	0.07	0.11	0.15	0.16	0.19	0.19	99% co
	FM 73	1.03	0.04	0.07	0.12	0.13	0.14	0.16	0.17	99% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.3.13 Effect of Testing Conditions on Wedge Test Results

Results in the wedge test can vary greatly depending on the aging conditions. The testing condition used during the grit-blast deoxidation experiments was 140°F and 95-100% RH. However, early work using the nylon-pad deoxidation process revealed that testing at 140°F and 95-100% RH was too severe to show differences in processing steps. For that reason, a lower temperature testing condition of 120°F and 95-100% RH was used to detect differences in processing steps. This testing condition was used to evaluate the Australian silane surface preparation and a similar grit-blast/silane (GBS) surface preparation in the early 1990s[15]. Due to the success of fielded bonded joints prepared using GBS optimized via wedge tests at 120°F and 95-100% RH, these same testing conditions were used for work with the nylon-pad deoxidation process. However, in order to compare to grit-blast/sol-gel, results of the nylon pad process tested at 140°F and 95-100% RH were required.

Al 2024-T3 wedge test adherends were treated with the nylon-pad/sol-gel process, primed with BR 6747-1, and bonded with AF 163-2M adhesive. Wedge test panels were machined into specimens, measured for bondline thickness, and tested at 120°F and 95-100% RH as well as 140°F and 95-100% RH. Results are shown in Table 2.3-17.

Table 2.3-17: Effect of Testing Conditions on Nylon Pad Wedge Test Results

Wedge Test Conditions	Initial (in)	Cummulative Crack Growth (in)							Failure Mode*
		1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
120°F & 95-100% RH	1.10	0.07	0.10	0.11	0.18	0.18	0.21	0.23	97% co
140°F & 95-100% RH	1.09	0.05	0.11	0.15	0.22	0.26	0.29	0.33	86% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.3.14 Initial Bond Strength Results

In order to determine the initial strengths of bonded joints prepared using Boegel-EPII over a nylon-pad-abraded surface, tensile lap shear and floating roller peel tests were conducted without moisture conditioning. This was to ensure the initial strength of the nylon-pad-abraded bonded

joints treated with Boegel-EPII is similar to that of PAA-prepared bonded joints and analogous to the grit-blast/sol-gel evaluation in section 2.2.7.

Adherends composed of Al 2024-T3 were treated with the nylon-pad/sol-gel process varying the sol-gel wet time. Panels were primed with BR 6747-1, when required, and bonded with AF 163-2M adhesive. Lap shear testing was performed at –65°F, 70°F, and 180°F after a four-minute soak at temperature. Floating roller peel testing was performed at 70°F and –65°F. Published data from 3M Company[16] using AF 163-2M over CAA primed with EC-3917 were used as controls along with PAA panels primed with BR 6747-1 and cured according to the manufacturer's recommendations. Results are shown in Table 2.3-18. Specimens failed cohesively under each testing condition except –65°F floating roller peel. Those specimens exhibited roughly 80% cohesive failure. Location of the other failure (~20%) appeared to be within the primer, as verified through EDX analysis.

Table 2.3-18: Initial Bond Strength Results for Nylon-pad-abraded Specimens Treated with Boegel-EPII and Primed with BR 6747-1

Surface Preparation	Lap Shear Strength (psi) [% Co Failure]			Peel Strength (pli) [% Co Failure]	
	-65°F	70°F	180°F	-65°F	70°F
Nylon-Pad/Boegel-EPII/BR 6747-1	5429 [94% Co]	5471 [98% Co]	3934 [97% Co]	58.3 [80% Co]*	68.8 [100% Co]
Published data on CAA/EC-3917	6400	5700	3600	58.0	79.0

co: cohesive within the adhesive layer

* 20% failure within the BR 6747-1 primer layer

Conducting on-aircraft bonded repairs typically requires curing at lower temperatures than recommended by the adhesive manufacturers due to wide temperature spreads caused by "heat sinks" in the structure. Curing under vacuum pressure is also common in the field environment. Therefore, several sets of mechanical strength tests were conducted curing 0.06psf AF 163-2M under 15 inches Hg vacuum pressure in order to replicate field-level bonding conditions. Two adhesive cure cycles were evaluated using vacuum cure pressures, (1) the manufacturer's recommended cycle of 60 minutes at 250°F, and (2) 6 hours at 200°F. The same nylon-pad/sol-gel surface preparation used for the positive pressure testing was used for the vacuum testing except the primer cure cycle was varied between precure and cocure (section 2.3.9). Two lap shear and peel panels (10 specimens) were fabricated and tested for each condition, unless otherwise noted. Specimens fabricated using grit-blast/silane and primed with BR 127 were used as a field-level control process. Results of the lap shear testing for specimens cured at 250°F are shown in Table 2.3-19. Results of the lap shear testing for specimens cured at 200°F are shown in Table 2.3-20. There is no difference in lap shear strength due to surface preparation when using either of the two adhesive cure cycles. However, when the adhesive was cured at 200°F and tested at –65°F, the nylon-pad/sol-gel specimens exhibited large amounts of adhesive failure at the primer-adhesive interface, even when using the primer cocure method.

Results of the floating roller peel testing for panels cured at 250°F for 60 minutes are shown in Table 2.3-21. Results of the floating roller peel testing for panels cured at 200°F for 6 hours are shown in Table 2.3-22. When tested at ambient temperature (70°F), there appears to be little

difference in peel strength due to surface preparation, and all specimens failed cohesively. However, when tested at –65°F, the specimens fail in the primer layer and exhibit lower bond strengths. Although there is a wide range of peel strengths, there does not appear to be any trends associated with surface preparation. Specimens cured at 200°F exhibit lower peel strengths at both test temperatures when compared to specimens cured at 250°F.

Table 2.3-19: Lap Shear Strength when Cured for 60 Minutes at 250°F and 15in Hg

Surface Preparation	Bond Primer	Lap Shear Strength (psi) (%cohesive failure)					
		-65°F		70°F		180°F	
Grit-Blast/Silane	BR 127 (precured)	5701	(93% co)	4777	(98% co)	2857	(100% co)
		4617	(93% co)	4179	(98% co)		
Nylon Pad/Sol-Gel	BR 6747-1 (precured)	5102	(86% co)	4196	(100% co)	1808	(97% co)
		5491	(90% co)	4188	(98% co)	3931	(99% co)
Nylon Pad/Sol-Gel	BR 6747-1 (cocured)	5327	(96% co)	5354	(100% co)	3114	(98% co)
		5290	(95% co)	4651	(99% co)		

Table 2.3-20: Lap Shear Strength when Cured for 6 Hours at 200°F and 15in Hg

Surface Preparation	Bond Primer	Lap Shear Strength (psi) (% cohesive failure)					
		-65°F		70°F		180°F	
Grit-Blast/Silane	BR 127 (precured)	5473	(93% co)	5793	(100% co)	3548	(99% co)
		4883	(94% co)	5044	(100% co)		
Nylon-Pad/Sol-Gel	BR 6747-1 (precured)	5105	(36% co)	4911	(100% co)	3025	(100% co)
		5504	(93% co)	4827	(100% co)	3374	(100% co)
Nylon-Pad/Sol-Gel	BR 6747-1 (cocured)	4978	(35% co)	5005	(100% co)	3454	(100% co)
		4881	(20% co)	5092	(100% co)		

Table 2.3-21: Floating Roller Peel Strength when Cured for 60 Minutes at 250°F & 15in Hg

Surface Preparation	Bond Primer	Peel Strength (pli) (% cohesive failure)			
		-65°F		70°F	
Grit-Blast/Silane	BR 127 (precured)	64.7	(76% co)	67.9	(98% co)
		47.4	(18% co)	63.5	(100% co)
Nylon-Pad/Sol-Gel	BR 6747-1 (precured)	42.9	(14% co)	64.6	(98% co)
		50.5	(10% co)	68.2	(96% co)
Nylon-Pad/Sol-Gel	BR 6747-1 (cocured)	44.6	(10% co)	68.3	(98% co)
		39.3	(15 % co)	65.2	(97% co)

Table 2.3-22: Floating Roller Peel Strength when Cured for 6 Hours at 250°F and 15in Hg

Surface Preparation	Bond Primer	Peel Strength (pli) (% cohesive failure)			
		-65°F		70°F	
Grit-Blast/Silane	BR 127 (precured)	54.6	(90% co)	59.8	(96% co)
		49.7	(60% co)	57.4	(100% co)
Nylon-Pad/Sol-Gel	BR 6747-1 (precured)	36.5	(10% co)	54.9	(97% co)
		37.1	(5% co)	62.4	(100% co)
Nylon-Pad/Sol-Gel	BR 6747-1 (cocured)	32.1	not recorded	57.0	(98% co)
		25.8	(10% co)	53.2	(97% co)

2.4 Optimization of Sol-Gel Surface Preparation Using "Sandpaper" Surface Activation Techniques

The use of grit-blasting and nylon-pad abrading prior to application of Boegel-EPII solution provided adequate bond surfaces for adhesive bonding. Good initial strength and bond durability results were achieved using both deoxidation techniques (sections 2.2 and 2.3), with grit-blasting providing better wedge test results at 140°F and 95-100% RH. Nylon-pad deoxidation provides a significant benefit when compared to grit-blasting due to the lack of grit containment required during deoxidation. "Sandpaper" surface activation techniques were evaluated as another alternative to grit-blasting.

In order to optimize the parameters associated with activating the bonding surface and subsequent application of Boegel-EPII and bond primers, two designed experiments were conducted to determine significant processing factors. Since a major evaluation of processing parameters was conducted on the nylon-pad deoxidation process, a similar evaluation was not conducted using sandpaper deoxidation. Upon completion of the two designed experiments, initial strength testing was performed on bonded joints prepared with the resulting "optimal" process.

2.4.1 Sandpaper Deoxidation Designed Experiment #1

The first of two designed experiments evaluated eight processing factors as shown in Table 2.4-1. An L16 test matrix was designed and conducted to evaluate processing factors and interactions associated with performing a surface preparation using sandpaper to deoxidize the surface prior to application of Boegel-EPII solution.

Both Al 2024-T3 and Al 7075-T6 aluminum alloys were evaluated since both 2000 and 7000 series alloys are used in many aircraft applications and may differ significantly in their responses to sandpaper abrasion due to different hardness and alloying elements. All adherends were cleaned with acetone and wiped with lint-free wipes until no remaining trace of grease, dirt, or contamination was visibly present. Two types of abrasive paper were used in this experiment, Craftsman aluminum oxide (Al_2O_3) and Craftsman silicon carbide (SiC), both purchased from Sears. Two grades of abrasive paper were used, fine (220 grit) and coarse (120 grit). Two sanding methods were also used to abrade the panels, a manual or hand sanding method using a sanding block and an air-driven jitterbug (manufactured by National Detroit, Inc.). Panels were abraded for either 2 or 5 minutes. Boegel-EPII solution was brush applied for either 10 or 20 minutes and dried at ambient temperature (70°F) for either 30 or 60 minutes prior to application of primer. Boegel-EPII solution was applied within 10 minutes of deoxidation in all cases. BR 6747-1 primer was applied using a spray gun. Panels were dried at ambient temperature for 30 minutes and cocured with 0.06psf AF 163-2M adhesive for 60 minutes at 250°F and 35-40 psi in a portable autoclave. Wedge test panels were machined into specimens, measured for bondline thickness, and tested at 120°F and 95-100% RH. Results of the designed experiment analysis are shown in Figure 2.4-1.

Table 2.4-1: Processing Factors for Sandpaper Deoxidation Designed Experiment #1

Factor	Parameter #1	Parameter #2
Alloy	Al 2024-T3	Al 7075-T6
Abrasive type	alumina	SiC
Paper grade	fine	coarse
Sanding method	hand	jitterbug
Abrade time	2 min	5 min
Application method	brush	spray
Boegel EPII wet time	10 minutes	20 minutes
Dry time	30 minutes	60 minutes

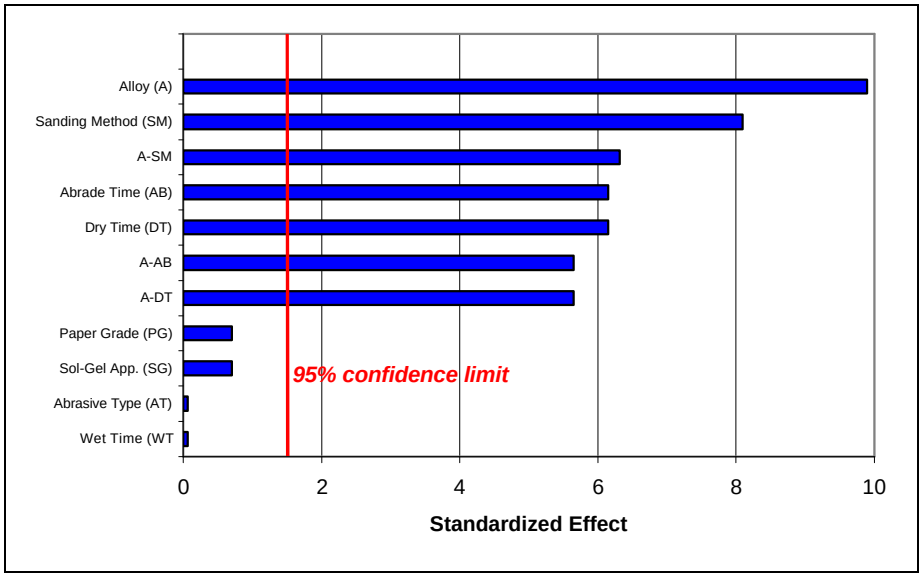


Figure 2.4-1: Significance of Sandpaper Deoxidation Processing Factors for the Sandpaper Designed Experiment #1

Four processing factors were deemed to be significant to the 95% confidence limit using failure mode as the evaluating criterion: alloy type, sanding method, abrade time, and Boegel-EPII dry time (Table 2.4-2). Experiments previously conducted using nylon-pad surface activation indicated the abrade-time factor (2.3.4) and Boegel-EPII dry-time factor (2.3.7) were insignificant. Although those two factors were determined to be significant in this designed experiment using sandpaper abrasion, it was doubtful that the mere use of sandpaper versus nylon pads caused the two factors to become significant since the two abrasion processes are so similar. Instead, it is more likely that the addition of the four insignificant factors (paper grade, application method, wet time, and abrasive type) resulted in the Anova analysis to be too sensitive to differences in test results due to increasing the number of degrees of freedom in the experiment. The first sandpaper designed experiment also showed that hand sanding provided better results than using the air-driven jitterbug. This did not match expected results since the jitterbug abraded the surface more aggressively and evenly than hand sanding. In any case, the better results gained with hand sanding did provide yet another option to field-level maintainers to perform an on-aircraft bonded repair without the use of specialized equipment. However,

hand sanding would be a difficult process to control due to the lack of quantifiable factors such as pressure and speed resulting in greater variability from application to application.

Table 2.4-2: Optimum Processing Parameters for Sandpaper Designed Experiment #1

Factor	Optimum Parameter
Alloy	Al 2024-T3
Sanding method	hand
Abrade time	2 minutes
Dry time	60 minutes
Paper grade	Insignificant
Application method	Insignificant
Boegel EPII wet time	Insignificant
Abrasive type	Insignificant

Alloy type was the most significant factor. Al 2024-T3 wedge test panels performed better than Al 7075-T6 wedge test. This was likely due to the difference in hardness between the two alloys. Al 2024-T3 has a Brinell hardness[17] of 120 Bhn[18] compared to the Brinell hardness of Al 7075-T6 of 150 Bhn[19]. The softer of the two alloys, Al 2024-T3, would be easier to abrade, thus yielding a rougher surface. The rest of the processing factors were deemed to be insignificant. The results of wedge test specimens processed with the "optimum" processing parameters from Table 2.4-2 are shown in Table 2.4-3 and compared to the results of the worst-performing wedge test specimens. Even with "optimum" processing conditions, the experiment was unable to provide failure modes above 95% cohesive. Due to the inferior results of the "optimized process" from the first designed experiment compared to nylon-pad/sol-gel, a second designed experiment was conducted using different processing parameters in the hopes of finding a better process that yielded improved results.

Table 2.4-3: Comparison of Wedge Test Results from Sandpaper Designed Experiment #1

Sandpaper Process	Initial (in)	Cummulative Crack Growth (in)					Failure Mode*
		1 hr	8 hr	24 hr	7 days	28 days	
Optimum	1.12	0.03	0.05	0.12	0.16	0.21	94% co
Worst Performing	1.13	0.05	0.06	0.12	0.26	0.74	0% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.4.2 Sandpaper Deoxidation Designed Experiment #2

The second sandpaper deoxidation designed experiment evaluated several different processing factors (Table 2.4-4). Instead of evaluating different sanding methods as in the first designed experiment, a pneumatic 5-inch diameter random orbital sander (Dynabrade Model 57016) was used to abrade the surface for all wedge test panels. A single type of abrasive paper was used for this evaluation, Norton Company™ 5-inch diameter self-sticking sanding discs. Two different solvents were used to degrease adherends, acetone and isopropyl alcohol (IPA). Two grit sizes of aluminum oxide were used for abrading, 220-grit and 120-grit. Another processing factor evaluated whether solvent wiping the bond surface after the sanding step provided any benefit. The amount of time between the sanding step and application of Boegel-EPII solution (post-

deoxidation time) was varied for an experimental factor to determine if a sanded surface had a maximum activated life. Two separate Cytec bond primers were used in this experiment, waterborne, chromated BR 6747-1 and waterborne, nonchromated BR 6757-1. Primer was applied using two different methods: spray using an HVLP gun and manual wiping using a lint-free cloth. Finally, panels were cured using either positive pressure or vacuum pressure. These processing factors and their interactions were all evaluated using an L16 test matrix that was composed of sixteen wedge test panels. All wedge test specimens were conditioned at 120°F and 95-100% RH.

Wedge test adherends were cleaned with the specified solvents in order to remove any contamination from the surface and then abraded with 3-inch 3M Company Scotch-Brite™ Roloc™ fine pads to obtain a baseline surface to begin the process. Adherends were solvent wiped again and deoxidized with Al_2O_3 sandpaper using the random orbital sander. Clean, dry nitrogen was used to operate the pneumatic orbital sander at a pressure of 50 psi. Compressed nitrogen was used to remove any debris remaining on the surface after deoxidation. Boegel-EPII solution was applied using an acid brush, and the surface was kept wet for 3 minutes. The adherends were dried at ambient laboratory conditions (70°F and 60% RH) for 30 minutes. After 30 minutes had elapsed, primer was applied to a nominal thickness of 0.1-0.3 mil, and dried at ambient temperature for 30 minutes. The primer was cocured with 0.06psf AF 163-2M adhesive in a portable autoclave for 60 minutes at 250°F and either 20 inches Hg vacuum pressure or 35 psi positive pressure. Cured wedge test panels were machined into specimens and measured for bondline thickness using an optical microscope. All specimens were tested at 120°F and 95-100% RH for 28 days.

Table 2.4-4: Processing Factors and Levels for Sandpaper Designed Experiment #2

Factor	**Level #1**	**Level #2**
Solvent type	Isopropyl Alcohol	Acetone
Sandpaper grit	220	120
Solvent wipe after deoxidization	no	yes
Post-deoxidization time	<10 min	60 min
Primer type	BR 6757-1	BR 6747-1
Primer application method	cloth	HVLP spray gun
Cure pressure	vacuum	positive pressure

This time, crack length measurements were used to determine the significance of factors and interactions to the 95% confidence limit using a design of experiments philosophy. Factors that exhibited a standardized effect greater than the 95% confidence limit were considered significant as shown in Figure 2.4-2. Three factors and two interactions were deemed to be significant. The three significant factors were primer type, primer application method, and cure pressure. Only one of the significant interactions could be identified, the interaction between the primer application method and the cure pressure. The other significant interaction term was unidentifiable because the designed experiment compounded two interaction terms. Two possible interactions existed and none of the factors contained in those interactions were deemed

to be significant in the experiment by themselves. No method of determining which of the possible interactions was actually significant existed. The "optimum" set of processing parameters for this experiment included spray-applied BR 6747-1 primer and vacuum-cure. The specimens that were processed using a bond primer (spray applied) and cured under vacuum exhibited the highest percentage of cohesive failure and the smallest amount of crack growth. Results of the best and worst performing wedge test panels from this experiment are shown in Table 2.4-5. There is a drastic difference in wedge test performance due to the significant processing factors and interactions evaluated in this designed experiment. All other processing factors and interactions were considered to be insignificant. These included solvent type, sandpaper grit, solvent wipe after sanding, and time between sanding and application of Boegel-EPII solution.

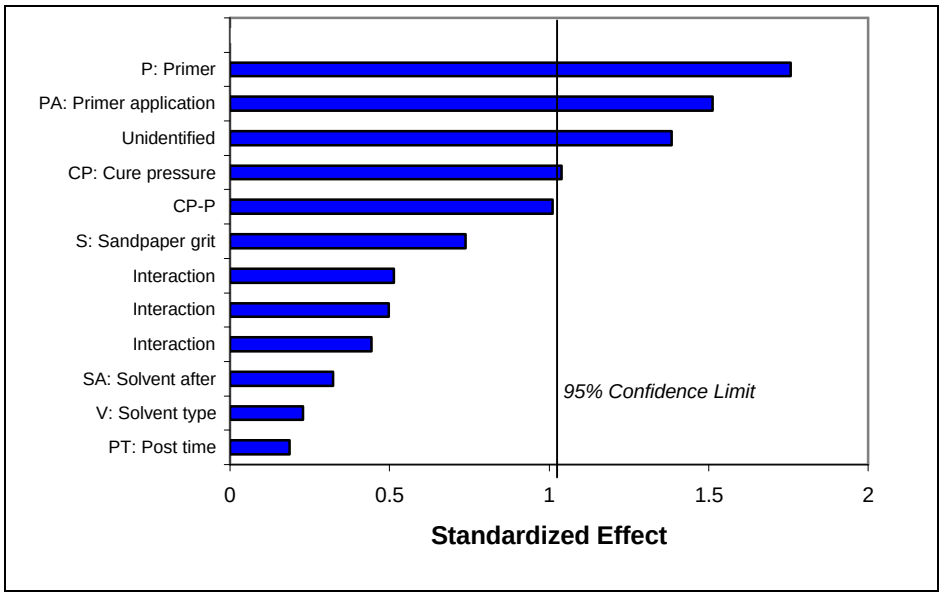


Figure 2.4-2: Significance of Processing Factors and Interactions for the Second Sandpaper Designed Experiment

Table 2.4-5: Comparison of Wedge Test Panels from Sandpaper Designed Experiment #2

Sandpaper Process	Initial (in)	Cummulative Crack Growth (in)							Failure Mode*
		1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
Optimum	1.15	0.05	0.09	0.13	0.14	0.14	0.15	0.15	96% co
Worst Performing	1.20	0.07	0.09	0.15	0.23	0.45	0.57	0.69	0% co

* co: cohesive failure within the adheive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

Wedge test specimens primed with BR 6757-1 exhibited interfacial failure modes between the primer and metal. Wedge test specimens primed with BR 6747-1 exhibited a higher percentage of cohesive failure and shorter crack lengths than the specimens primed with BR 6757-1. A number of the specimens primed with BR 6747-1 exhibited 90-95% cohesive failure versus wedge test specimens exhibiting complete adhesional failure when primed with BR 6757-1.

Priming using the cloth-wipe process proved to be detrimental to wedge test performance. When the primer was applied with the cloth, specimens exhibited interfacial failure modes as shown in Figure 2.4-3. The experiment showed that specimens primed using an HVLP spray gun exhibited higher amounts of cohesive failure. This pertains to panels that were primed with BR 6747-1 since the specimens primed with BR 6757-1 exhibited interfacial failure modes regardless of the primer application method. It is possible that the 30-minute ambient temperature dry time was insufficient to fully dry the Boegel-EPII coating prior to wipe application of the primer. The sol-gel coating may have been damaged or partially removed while wiping the waterborne primer. This same problem might not be noticed with a spray application of the primer since this deposits the primer on the surface without touching the bond surface.

Figure 2.4-3: Failure Mode Exhibited Using Cloth-Applied Primer

Wedge test specimens cured under vacuum exhibited better results than specimens cured with a positive pressure cure cycle. The best-performing wedge test specimens were cured under vacuum and primed with BR 6747-1 using an HVLP gun. When comparing those vacuum-cured specimens to similar specimens primed with BR 6747-1 using an HVLP spray gun and cured under positive pressure, the vacuum-cured specimens' failure modes were slightly more cohesive. The optimum vacuum-cured specimens exhibited 95% cohesive failures. The remaining 5% interfacial failure (between the primer and metal) occurred at the edges of the specimen. The positive-pressure wedge specimens exhibited approximately 90% cohesive failure with the small amount of interfacial failure occurring at the edges. However, the nicks at the edges of the specimens cured under positive pressure were larger than the nicks of the specimens cured under vacuum. Curing the adhesive under vacuum caused the formation of porosity within the adhesive bondline. Trapped porosity weakens the mechanical properties of the adhesive and reduces the amount of stress at the interface. When the wedge test specimens are cured with positive pressure, the adhesive exhibits stronger mechanical properties due to the lack of porosity. Since the adhesive is stronger, the crack tends to stress the interface more, which can lead to more interfacial failure in the wedge test specimens. It was seen in this experiment that the crack growth in the vacuum-cured specimens was slightly higher than the specimens cured with positive pressure. Although the vacuum-pressure cure cycles appear to provide a benefit in the wedge test for the sol-gel surface preparation, it is not a valid comparison to the positive-pressure-cured specimens since the properties of the adhesive are not the same in both tests. The purpose of evaluating the cure pressure was to ensure that curing under vacuum

pressure did not lead to a detrimental effect on the durability of the bond. Vacuum cure cycles are typically used in the field for on-aircraft repairs due to the difficulty associated with applying positive pressure on aircraft.

Specimens were fabricated with Al 2024-T3 adherends for tensile lap shear and floating roller peel testing at ambient temperature. Specimens deoxidized with sandpaper, treated with Boegel-EPII solution, and primed with BR 6747-1 using the "optimized" process derived from the second designed experiment were compared to specimens prepared with PAA and primed with BR 127.

Adherends were cleaned with acetone in order to remove organic contamination from the surface. The wedge test panels were abraded with fine grade 3-inch 3M Company Scotch-Brite™ Roloc™ pads to obtain a baseline surface to begin the surface preparation. Wedge test panels were solvent wiped again and deoxidized with varying grits of Al_2O_3 sandpaper using a random orbital sander. Clean, dry nitrogen was used to operate the pneumatic orbital sander at a pressure of 50 psi in order to prevent surface contamination from dirty and oily compressed air lines. Compressed nitrogen was used to remove debris remaining on the surface after deoxidation. Boegel-EPII solution was applied using an acid brush, and the surface was kept wet for 3 minutes. The wedge test panels were dried at ambient laboratory conditions (70°F and 60% RH) for 30 minutes. After drying, primer was spray applied to a nominal thickness of 0.1-0.3 mils and dried at ambient temperature for 30 minutes. The primer was cocured with 0.06psf AF 163-2M adhesive in a portable autoclave for 60 minutes at 250°F and either 20 inches Hg vacuum pressure or 35 psi positive pressure. Cured panels were machined into specimens and measured for bondline thickness prior to testing using an optical microscope. Results for are shown in Table 2.4-6.

Table 2.4-6: Ambient Temperature Initial Bond Strength Results for Sandpaper-Abraded Specimens Treated with Boegel-EPII and Primed with BR 6747-1

Surface Prep	**Lap Shear (psi)**		**Peel (pli)**	
	Vacuum	***Positive Pressure***	***Vacuum***	***Positive Pressure***
PAA/BR 127	3060	5816	60.9	53.4
Sandpaper / Boegel-EPII	3191	6077	63.3	60.2

All failure modes were cohesive and all the strengths were very similar for specimens prepared with PAA/BR 127 and sandpaper deoxidation/Boegel-EPII/BR 6747-1 treatment. The large reduction in lap shear strength when cured under vacuum pressure also explains the improved wedge test results due to vacuum curing discussed in Section 2.4.2.

2.4.3 Systematic Abrasive Media Study

Several early studies highlighted the difference in performance when using different abrasive media and tools to deoxidize the aluminum surface prior to sol-gel application. To that regard, a systematic study was carried out to look at the surface chemistries of the different abrasive products and compare them directly to the performance that is achieved in a controlled

experiment. Seven different abrasive media were used. Peel, wedge crack extension, and double cantilever beam (DCB) test data were generated for all seven candidates. In addition, Electron Spectroscopy for Chemical Analysis (ESCA), scanning electron microscopy (SEM), and profilometry were performed on aluminum substrates treated with the abrasive media as well as control specimens. ESCA and scanning electron microscopy were also conducted on abrasive media samples.

2.4.3.1 Test Matrix

To determine effects on surface contamination and morphology, Al 2024-T3 panels were prepped with the different sandpapers and abrasive media shown in Table 2.4-7.

Table 2.4-7: Abrasive Media Matrix

No.	Sandpaper/Abrasive Media	Abrasive Medium	Method
1	3M 210U-P180	Al_2O_3	Random Orbital Sander
2a	Merit SK-62-P180 Shur-Stik	Al_2O_3	Random Orbital Sander
2b	Merit SK-62-P120 Shur-Stik	Al_2O_3	Random Orbital Sander
3	Merit 120 Zirc Plus Power-Lock Discs	ZrO_2	Die Grinder
4	3M 268L #180 alumina, 5in disc, Type D	Al_2O_3	Random Orbital Sander
5	3M 326U #220 alumina	Al_2O_3	Random Orbital Sander
6	Standard Abrasives A/O Xtra, #180 grit, Type I Lockit	Al_2O_3	Die Grinder
7a	Scotch-Brite™ medium Roloc™ disc (maroon)	Cubitron™ Grain	Die Grinder
C1	Solvent Wipe	N/A	N/A
C2	Chemical Deoxidation	N/A	N/A

Two specimens were prepared, sized 6in x 6in x 0.125in, with each surface preparation. These samples were used for ESCA, SEM, and profilometry analyses. In parallel, specimens were fabricated using the same abrasives described above in order to conduct strength and durability testing (wedge, DCB, climbing drum peel) to determine differences in Al 2024-T3 specimens. Boegel-EPII solution, precured Cytec BR 6747-1, and 3M AF163-2OST were used to fabricate the performance trial specimens. The process steps used are shown in Table 2.4-8.

Table 2.4-8: Process Method Used to Prepare Sol-Gel Test Specimens

Step #	Process
1	Solvent wipe with MEK followed by acetone until cheesecloth is clean
2	Abrade with random orbital sander or die grinder
3	Blow off loose particles with clean dry air
4	Spray surfaces with Boegel-EPII (AC-130 kit) for 2-3 minutes, keeping surfaces wet. Apply sol-gel within 30 minutes of abrasion
5	Dry at ambient temperature for one hour
6	Spray apply adhesive bond primer, Cytec BR 6747-1
7	Apply adhesive, AF 163-2M
8	Cure at 250°F in autoclave at 45 psig for 60 to 75 minutes

The abrasion process was carried out using a random orbital sander or a die grinder, both fitted with a filtered rear exhaust (Table 2.4-9). The process involved sanding with the candidate abrasive paper or pad for one to two minutes over approximately 6 in x 6 in sections. The sander was guided from side to side across the entire 6 in x 6 in area and abraded in a perpendicular direction to achieve one cross-coat (Figure 2.4-4). The sandpaper was changed when it became worn, as evidenced by tears, seizing of the tool, and clogging. At a minimum, one fresh piece of sandpaper for each 6 in x 6 in area was used. The sanding speed was adjusted in particular experiments and tended to range from a 1 to 2 minute period over a 6 in x 6 in area.

Table 2.4-9: Surface Preparation Tool Details for Sandpaper Variation Study

Surface Prep Tool	Abrasive diameter	Speed
Random Orbital Sander	3 in – 5 in	10,000 orbits/min
Die Grinder	5in with 3in backing pad	20,000 rpm

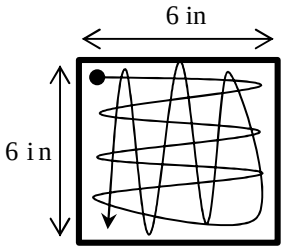
Area/Sanding Pattern	
Sandpaper Changeout	1 piece/36 in^2
Time Sandpaper Used	1-2 min/36 in^2

Figure 2.4-4: Sanding Procedures Used in Sol-Gel Testing

2.4.3.2 <u>Performance Test Results</u>

The results for climbing drum peel testing per Boeing BSS7206[20] are shown in Table 2.4-10.

Table 2.4-10: Peel Strength Results for Different Abrasive Surface Preparations

No.	Surface Preparation	Dry Peel Strength (in-lb/in)	Failure Mode (% co)
1	3M 210U-P180	84	100
2a	Merit SK-62-P180	86	100
3	Merit 120 Zirc Plus	89	100
4a	3M 268L 80 Micron, 5in disc, Type D	88	100
5	3M 326U #220 alumina	89	100
6	Standard Abrasives A/O Xtra, #180 grit, Type I Lockit	90	100
7a	Scotch-Brite™ medium Roloc™ disc (maroon)	85	100

co: cohesive failure within the adhesive layer

No distinct differences were seen in the dry peel strengths of the specimens with any of the abrasive media and techniques tested here, indicating that there was not gross contamination of the surface using the abrasives and methods in this iteration. However, there were subtle differences in the wedge test performance of these specimens, which is shown in Table 2.4-11. Sample #5, abraded with the 3M 326U yielded a greater crack growth and more adhesional failure than the other sandpapers. This sandpaper was the original sandpaper tested from the historical testing, which was designed for use with nonmetallic materials. The variability in the performance of the specimen abraded with the 3M 326U confirmed that there is most likely some residue smeared on the surface using this abrasive paper, which accounts for the degradation in the hot/wet properties. In general, the 3M abrasive papers gave slightly longer crack lengths than the Merit abrasive papers, but the failure modes after 4 weeks were fairly similar.

Additionally, the failure modes of the Scotch-Brite™-abraded specimens, #7a, were less acceptable in hot/wet wedge crack testing than those for the majority of the sandpapers. Better results have been achieved in other testing using the Scotch-Brite™ materials (Table 2.3-3).

Table 2.4-11: Series A Wedge Test Data for Samples Exposed to 140°F and >98% RH

No.	Surface Preparation	Initial Crack (in)	Cumulative Crack Growth (in)			Failure Mode (%co)
			24hr	168hr	672hr	
--	PAA	1.20	0.03	0.05	0.08	100
1	3M 210U-P180	1.14	0.16	0.23	0.25	98
2a	Merit SK-62-P180	1.18	0.12	0.12	0.16	98
3	Merit 120 Zirc Plus	1.18	0.13	0.13	0.14	98
4	3M 268L 80 Micron, 5in disc, Type D	1.18	0.13	0.22	0.24	98
5	3M 326U #220 alumina	1.21	0.15	0.27	0.30	85
7a	Scotch-Brite™ medium Roloc™ disc (maroon)	1.18	0.14	0.23	0.25	88

Double cantilever beam specimens were also fabricated in parallel with the wedge test specimens. These were abraded with the specified media, treated with Boegel-EPII, primed with BR 6747-1 (precured), and bonded with AF 163-2M adhesive. The DCBs were conditioned in a 140°F, >98% RH environment. Environment Crack Extension Force (G_{Iscc}) was calculated for 5 and 15 weeks of exposure; results are shown in Table 2.4-12. The DCB test tends to yield lower percentage cohesive failure modes than the wedge test, so it was not surprising the failure modes ranged from 40 to 83 percent cohesive for the lengthy 15-week exposure at 140°F.

Table 2.4-12: Double Cantilever Beam Results Summary

No.	Surface Preparation	Initial Crack Length (in)	5-week Exposure		15-week Exposure		Percent Cohesive Failure
			Crack Length (in)	G_{Iscc} (in-lb/in^2)	Crack Length (in)	G_{Iscc} (in-lb/in^2)	
1	3M 210U-P180	3.05	4.59	4.25	5.18	2.69	40
2	Merit SK-62-P180	3.08	4.43	4.85	5.04	2.98	55
3	Merit 120 Zirc Plus	3.04	4.34	5.20	4.75	3.74	83
4	268L 80um 5in disc Type D	3.11	4.34	5.21	4.90	3.31	41
5	3M 326U#220 alumina	3.16	4.28	5.48	4.66	4.00	72
6	Std. Abr. A/O Xtra #120 grit	3.13	4.21	5.82	4.64	4.08	62
7	Scotch-Brite™ med. Roloc™	2.99	4.12	6.33	4.72	3.82	57

Std. Abr.: Standard Abrasives

2.4.3.3 Surface Analysis

An ESCA survey-scan was performed on sample specimens treated with the candidate abrasive media to determine the ability to remove the outer oxide layer and the relative cleanliness of the abraded surface. Data for the sandpaper samples and the solvent-wiped and chemically deoxidized controls are shown in Table 2.4-13. The reduction of magnesium and increase of aluminum at the surface between the solvent-wiped and abraded samples indicates that the bulk alloy has been exposed. The source of the higher carbon level on the surface of the Scotch-Brite™ abraded and chemically deoxidized panels cannot be attributed to a specific source from this data alone. Possible sources include organic material from the Scotch-Brite™ pad or excess carbon pickup on a highly activated surface.

Table 2.4-13: ESCA Data for Aluminum Substrates with Different Surface Preparations

No.	Surface Preparation	Atomic %				
		Carbon	Oxygen	Aluminum	Magnesium	Other
---	Solvent Wiped	36.1	34.3	6.2	23.2	0.2
1	3M 210U-P180	16.2	45.0	35.7	1.7	1.3
2	Merit SK-62-P180	14.5	45.1	36.8	2.0	1.6
3	Merit 120 Zirc Plus	12.9	43.7	38.5	2.4	2.6
4	268L 80um 5in disc Type D	15.6	44.6	36.6	2.4	0.7
5	3M 326U#220 alumina	13.6	44.8	37.5	2.4	1.6
6	StAb A/O Xtra #120 grit	13.9	44.0	38.1	2.5	1.5
7	Scotch-Brite™ medium Roloc™	29.2	35.6	32.9	0.8	1.4
---	Chemical Deoxidation	25.8	36.2	24.9	0.6	11.5

ESCA was performed on abrasive media numbers 1, 2, 6, and 7 before and after use to determine changes, if any, to the media. The only significant difference between the before and after

ESCA numbers was a slight pickup of aluminum and/or magnesium, which would be expected. SEM photomicrographs were taken of each sample to observe the surface morphology. Representative photomicrographs at 50X and 500X are shown in Figure 2.4-5. The following observations were made from the photomicrographs and EDX analyses:

- The difference in gross morphology due to prep method (die grinder vs. random orbital sander) is evident at 50X (samples 1, 2, 4, and 5 vs. samples 3, 6, and 7);
- #1 (3M 210U-P180) sandpaper may be degrading and burnishing substrate;
- #3 (Merit 120 Zirc Plus) showed no apparent zirconia contamination either by EDX or ESCA even though the hardness of zirconia is lower than that of alumina - it is the only zirconia medium included in this study, all others are alumina - this surface preparation has done well in previous performance tests
- #4 (268 80um 5in disc Type D) has finer features but more loose “junk” on the surface;
- #5 (3M 326U #220 alumina) exhibited definite burnishing;
- Iron (which was not detected with ESCA) was detected by EDX in some of the samples, most notably #1.

Photomicrographs were also taken of all the candidate media before and after use. Summary photos are shown in Figure 2.4-6. The following observations were made:

- Density of abrasive grit varies greatly between media;
- Embedding of aluminum particles was seen in numbers 1, 3, 4, and 6 after use;
- Grit high points were damaged or broken down during use in numbers 2, 3, and 6;
- Some binders exhibited cracking before and/or after use; and
- #4 exhibited holes or bubbles in the binder that were more apparent after use.

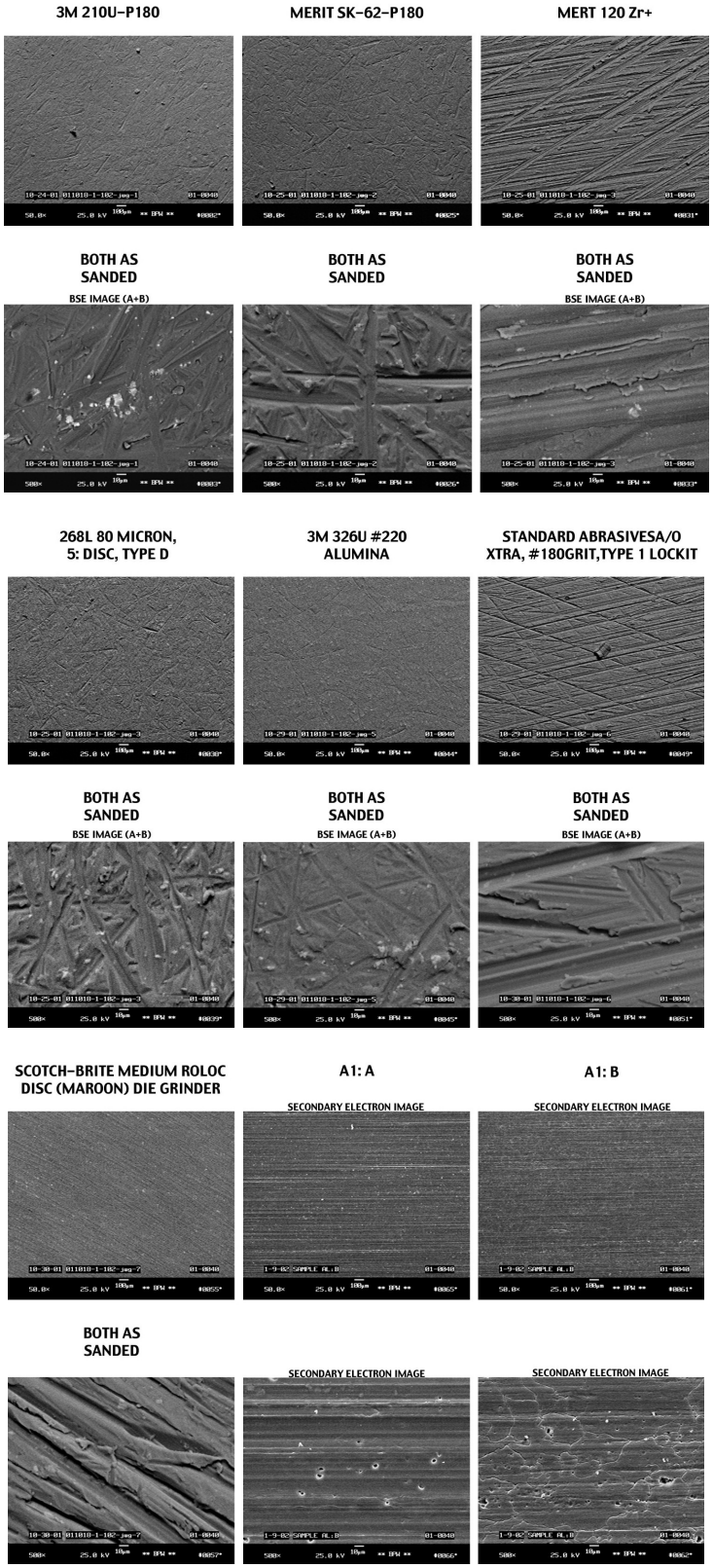


Figure 2.4-5: Photomicrographs of Aluminum Substrates After Deoxidation with Various Media

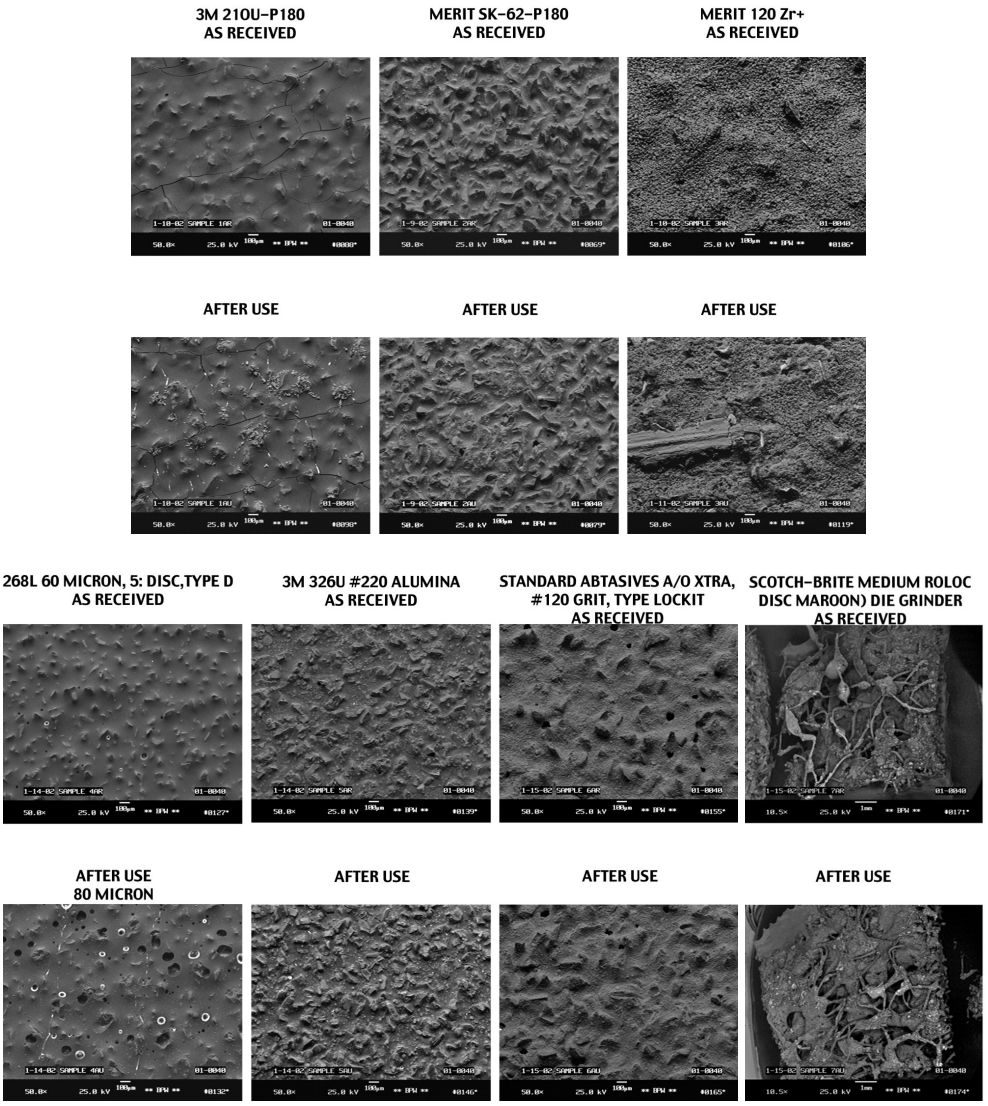


Figure 2.4-6: Photomicrographs of Abrasive Media Before and After Use

The surface roughness of each of the abraded aluminum samples was measured using a Wyko NT2000 Optical Profiler. This equipment uses vertical scanning interferometry to measure the profile of surfaces. It has a 10 x 0.5 objective and reports roughness values in μin. Table 2.4-14 shows a comparison of roughness values for the test matrix. Figure 2.4-7 shows the results of this analysis with a key to the different roughness values reported.

The differences in abrasion pattern seen in the photomicrographs between the random orbital sander (numbers 1, 2, 4, and 5 from Table 2.4-13) and the die grinder (numbers 3, 6, and 7) are also very apparent in the surface maps shown in Figure 4.3-6. Also interesting is the similarity in roughness values between similar media and tools, i.e. numbers 1, 2, and 4 (random orbital sander), and numbers 6 and 7 (die grinder). Number 3 (Merit Zirc Plus 120 grit) had an unusually deep profile, possibly owing to the zirconia grit, as number 6 is also120 grit (alumina). Number 5 had an unusually low profile, probably due to the fact that the paper is designed for use with wood, not metal.

Table 2.4-14: Summary of Aluminum Panel Roughness Values

	Sample #						
Value	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Ra	28.06	32.31	94.91	35.91	16.96	52.88	59.14
Rp	370.16	438.82	712.57	391.68	180.80	300.01	218.18
Rq	38.07	44.29	127.94	48.21	22.50	67.55	77.52
Rt	793.27	835.00	1361.52	793.89	353.30	876.96	568.31
Rv	-423.11	-396.17	-648.95	-402.20	-172.50	-576.95	-350.13

Note: Die grinder sample columns are shaded.

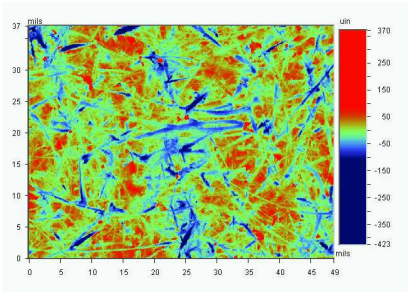
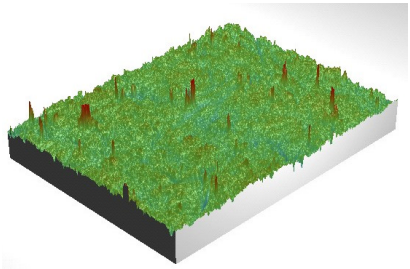
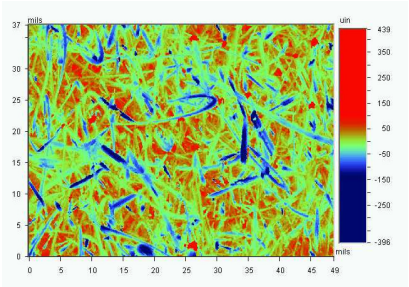
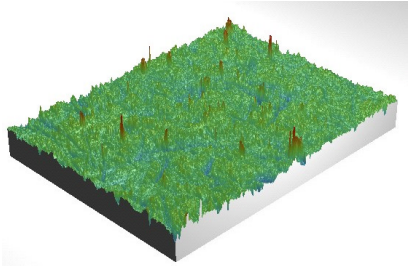
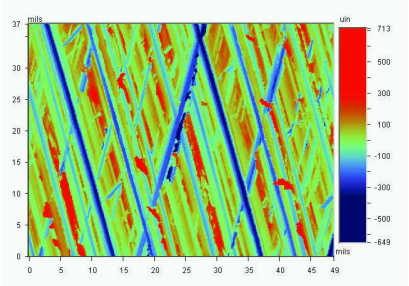
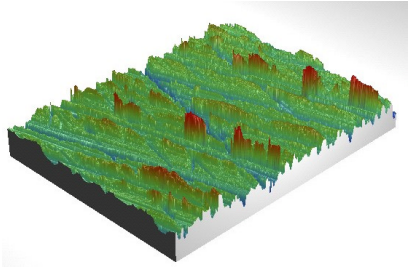
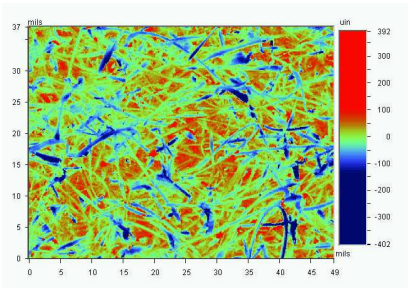
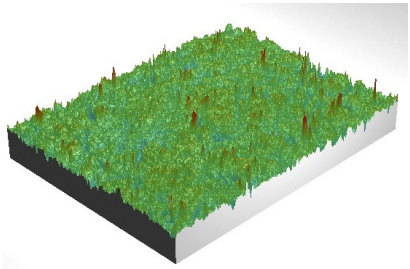
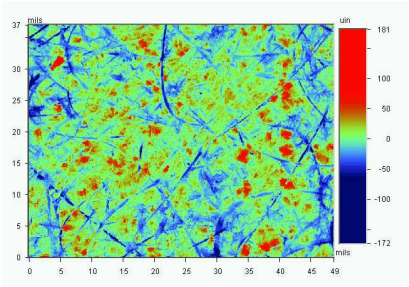
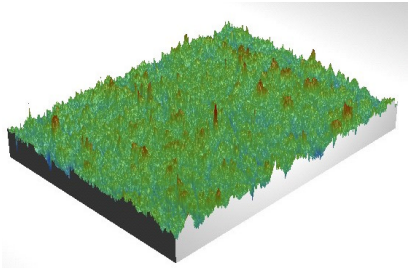
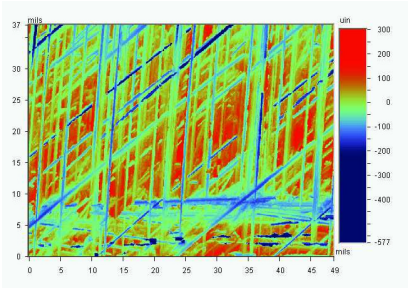
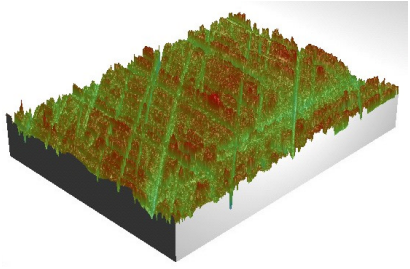
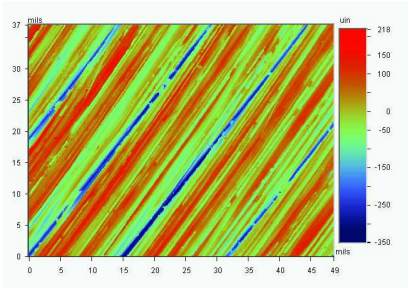
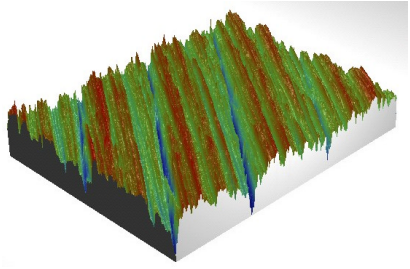
3M 210U-P180 Ra 28.06 Rp 370.16 Rq 38.07 Rt 793.27 Rv -423.11		
Merit SK-62-P180 Ra 32.31 Rp 438.82 Rq 44.29 Rt 835.00 Rv -396.17		
Merit 120 Zirc+ Ra 94.91 Rp 712.57 Rq 127.94 Rt 1361.52 Rv -648.95		

Figure 2.4-7: Surface Profile Results for Aluminum Substrates Abraded with Various Media

3M 268L 80 micron Ra 35.91 Rp 391.68 Rq 48.21 Rt 793.89 Rv -402.20		
3M 326U #220 alumina Ra 16.96 Rp 180.80 Rq 22.50 Rt 353.30 Rv -172.50		
Standard Abrasives A/O Xtra #120grit Ra 52.88 Rp 300.01 Rq 67.55 Rt 876.96 Rv -576.95		
Scotch-Brite™ Medium Roloc™ Disc Ra 59.14 Rp 218.18 Rq 77.52 Rt 568.31 Rv -350.13		

KEY:

Ra, Roughness Average: The arithmetic average height calculated over the entire array.

Rp, Maximum Profile Peak Height: The distance between the mean line and the highest point over the evaluation length.

Rq, Root Mean Square: The root mean square average height calculated over the entire measured array.

Rt, Maximum Profile Height: The distance between the highest and lowest points over the evaluation length.

Rv, Maximum Profile Valley Depth: The distance between the mean line and the lowest valley over the evaluation length.

Figure 2.4-7: Surface Profile Results for Aluminum Substrates Abraded with Various Media (Continued)

2.4.4 Sanding Temperature Study

Thermocouples were attached to aluminum samples during and after sanding to determine the temperature change of the substrate. Table 2.4-15 shows the test matrix and Figure 2.4-8 shows the measured temperature of the aluminum substrate. Thermocouple 1 was taped to the center of the back of the 6in x 6in x 0.020in specimen, and Thermocouple 2 was placed between the aluminum specimen and tool immediately after sanding/grinding. Samples 1, 2, 4, and 5 (random orbital sander) were sanded for 2 minutes using a cross coat technique in a typical wedge test specimen preparation. Samples 3, 6, and 7 were ground for 1 cross coat in a typical wedge test specimen preparation.

Table 2.4-15: Sanding Temperature Matrix

Sample No.	"Sandpaper"				Tool			
	Mfgr.	**Type**	**Grit**	**Diameter**	**Mfgr.**	**Type**	**Speed**	**Diameter**
1	3M	210U	P180A	5 inch	DeWalt	ROS	10,500 rpm	5 inch
2	Merit	A/O SK-62	180	5 inch	DeWalt	ROS	10,500 rpm	5 inch
3	Merit	Zirc Plus	120	3 inch	Myton	D.G.	22,000 rpm	3 inch
4	3M	268L	60 u	5 inch	DeWalt	ROS	10,500 rpm	5 inch
5	3M	326U	220	5 inch	DeWalt	ROS	10,500 rpm	5 inch
6	Std. Abr.	A/O Xtra	120	3 inch	Florida	D.G.	25,000 rpm	2 inch
7	3M	Scotch-Brite™	medium	2 inch	Florida	D.G.	25,000 rpm	2 inch

Std. Abr.: Standard Abrasives; ROS: Random Orbital Sander; D.G.: Die Grinder

Again, there is a clear difference in the samples abraded using the die grinder and those abraded using a random orbital sander. However, in laboratory studies the performance testing did not pick up the differences in the process techniques. It is possible that these variations are magnified in an uncontrolled setting and may result in greater differentiation.

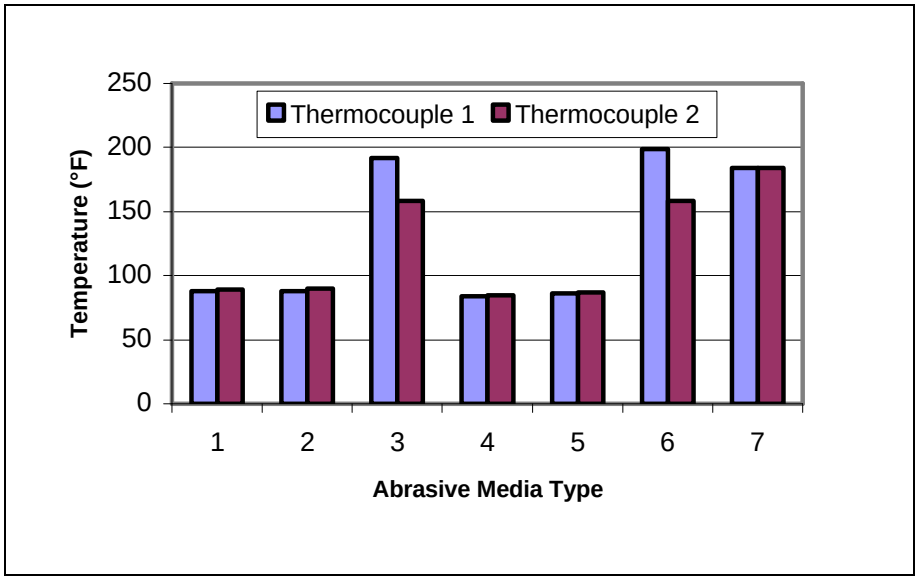


Figure 2.4-8: Temperatures for Aluminum Substrates Abraded with Various Media

2.4.5 Sanding Variation Study

A test plan was conducted to evaluate how sanding styles among personnel affect the adhesive bonding performance of sol-gel coated aluminum. In addition, sets of wedge test panels were prepared by wet sanding with water and with sol-gel. The details of the sample preparation are shown in Table 2.4-16. The results of sanding variation and wet abrade tests are presented in Table 2.4-17.

Table 2.4-16: Test Matrix for Sanding Style Variations and Wet Abrasion

Specimen	Substrate	Surf Prep	Sanding Time/Method	Surf Treat	Primer	Adhesive
D60-1	2024-T3 bare	#220 Al_2O_3 sanded	Demo 1, 3 minutes, fast stroke	Spray Boegel-EPII	BR 6747-1	AF 163-2M
D60-2	2024-T3 bare	#220 Al_2O_3 sanded	Demo 2 (~20 seconds, fast stroke)	Spray Boegel-EPII	BR 6747-1	AF 163-2M
D60-3	2024-T3 bare	#220 Al_2O_3 sanded	Wet sand with water	Spray Boegel-EPII	BR 6747-1	AF 163-2M
D60-4	2024-T3 bare	#220 Al_2O_3 sanded	Wet sand with sol-gel	Spray Boegel-EPII	BR 6747-1	AF 163-2M

Table 2.4-17: Results of Sanding Style Variations and Wet Abrade

Sanding Style	Initial (in)	Cumulative Crack Growth (in)					Failure Mode*
		24hr	168hr	336hr	504hr	672hr	
D60-1, #220 sand, 3minutes, fast stroke	1.18	0.02	0.02	0.15	0.15	0.15	88% co
D60-2, #220 sand, 20 seconds, fast stroke	1.22	0.14	0.14	0.14	0.14	0.14	96% co
D60-3, #220 sand, wet sand with water	1.24	0.20	0.20	0.30	0.30	0.30	84% co
D60-4, #220 sand, wet sand with sol-gel	1.22	0.18	0.18	0.18	0.18	0.18	90% co

*co: cohesive within the adhesive layer

Wedge test data indicate the more thorough sanding methodology employed in Demo 1 and the quicker, less aggressive sanding employed in Demo 2 in this study gave approximately the same performance. Sanding with water appeared to degrade the bondline, as was confirmed with earlier data on this technique. However, sanding with the sol-gel solution did not seem to be deleterious in this study.

2.4.6 Reproducibility of Individual Sanding Techniques

Additional tests were conducted to observe changes in bond performance due to differences in individual sanding techniques, and to evaluate the reproducibility of the bond performance per individual. A baseline sanding process was designated where each 6-inch x 6-inch area was sanded with one fresh piece of #220 alumina sandpaper for a two-minute period. Four different

test technicians were used to evaluate the process robustness and reproducibility. Each individual sanded three sets of wedge test panels on each day over a three-day period. Substrates were bare Al 2024-T3 sanded with #220 Al_2O_3 using a random orbital sander. Specimens were sprayed with Boegel-EPII, air-dried, spray-primed with Cytec BR 6747-1, and bonded with AF 163-2M. The wedge test results are presented in Table 2.4-18. The effect of slight variations in sanding techniques among personnel appears to be minimal.

Table 2.4-18: Wedge Test Results of Reproducibility Evaluation Among Individuals

Sander	Hours of Exposure to 140°F and >98%RH / Total Crack Length (inches)						Crack Extension, 7 days (inches)	Failure Mode
	0	1	24	96	120	168		% co
RA-1-1	1.20	1.23		1.40		1.40	0.20	97
RA-1-2	1.23	1.26		1.37		1.40	0.17	97
RA-1-3	1.28	1.31		1.47		1.47	0.19	98
RA-2-1	1.23	1.28		1.39		1.39	0.16	98
RA-2-2	1.20	1.26		1.39		1.39	0.19	98
RA-2-3	1.29	1.34		1.47		1.47	0.18	98
RA-3-1	1.23	1.29		1.42		1.42	0.19	98
RA-3-2	1.24	1.29		1.41		1.45	0.21	98
RA-3-3	1.21	1.26		1.41		1.41	0.20	97
JF-1-1	1.27	1.31	1.37		1.45	1.45	0.18	98
JF-1-2	1.23	1.25	1.36		1.37	1.40	0.17	97
JF-1-3	1.27	1.31	1.40		1.47	1.47	0.20	98
JF-2-1	1.21	1.23	1.33		1.38	1.40	0.19	98
JF-2-2	1.23	1.27	1.35		1.37	1.43	0.18	98
JF-2-3	1.24	1.27	1.37		1.41	1.42	0.18	98
JF-3-1	1.22	1.26	1.33		1.36	1.36	0.14	97
JF-3-2	1.25	1.27	1.33		1.37	1.37	0.12	97
JF-3-3	1.23	1.26	1.37		1.39	1.40	0.17	96
MG-1-1	1.23	1.25		1.43		1.44	0.21	98
MG-1-2	1.17	1.21		1.34		1.34	0.17	98
MG-1-3	1.23	1.27		1.38		1.38	0.15	99
MG-2-1	1.22	1.26		1.39		1.44	0.22	99
MG-2-2	1.22	1.26		1.40		1.40	0.18	97
MG-2-3	1.23	1.28		1.41		1.44	0.21	96
MG-3-1	1.24	1.28		1.43		1.43	0.19	98
MG-3-2	1.30	1.34		1.41		1.45	0.15	97
MG-3-3	1.26	1.29		1.34		1.42	0.16	98
DM-1-1	1.25	1.28	1.36		1.46	1.51	0.26	96
DM-1-2	1.24	1.27	1.39		1.45	1.45	0.21	95
DM-1-3	1.22	1.25	1.36		1.42	1.43	0.21	96
DM-2-1	1.19	1.23	1.34		1.42	1.46	0.27	95
DM-2-2	1.26	1.30	1.36		1.43	1.43	0.17	98
DM-2-3	1.23	1.26	1.29		1.43	1.43	0.20	96
DM-3-1	1.21	1.26	1.37		1.40	1.40	0.19	96
DM-3-2	1.26	1.28	1.36		1.41	1.41	0.15	96
DM-3-3	1.23	1.27	1.34		1.41	1.42	0.19	96

co: cohesive failure within the adhesive layer

2.4.7 Clad Aluminum Evaluation

Studies were conducted to determine if the sol-gel process would be effective on clad aluminum surfaces. Wedge test data on clad Al 2024-T3 exhibited favorable results, similar to the bare alloy, (Table 2.4-19). During preparation of the wedge test panels, no attempt was made to remove the pure aluminum layer (cladding) from the substrates before they were roughened using three different techniques: grit blasting with 50-micron alumina as well as abraded with medium (maroon) Scotch-Brite™ Roloc™ discs, and # 220 alumina paper.

Peel testing was also conducted to determine the effectiveness of sol-gel coatings to bond clad Al 2024-T3. Peel specimens were prepared from 2024-T3 bare and clad. Each group of samples was prepared using the different mechanical deoxidation techniques to determine how various surface roughening techniques might affect sample performance. Both floating roller peel and climbing drum peel tests were conducted. All peel test samples were spray-coated with Boegel-EPII for an application time of two minutes, primed with BR 6747-1, and autoclave bonded with AF 163-2M film adhesive. Table 2.4-20 and Table 2.4-21, for bare and clad respectively, list more details of the preparation, test conditions, and test results. The term "water spray" for some roller peel tests refers to the spray application of water to the crack tip region of specific roller peel samples over the course of the test. This is done to determine if the presence of water at the bond interface and crack tip reduces the test values.

In this case, peel testing of both the bare and the clad aluminum under ambient conditions exhibited very high peel strengths, indicative of this toughened epoxy adhesive system. At cold temperatures, the results were more variable, with the failure modes mixed at several interfaces. Primer still appeared to be present on these samples. The failure is suspected to have occurred within the primer layer rather than at the interface with the adhesive. The water spray testing gave reasonable numbers, also with mixed failure modes.

Table 2.4-19: Effect of Sol-Gel Surface Preparations on Clad Al 2024-T3

Process Conditions Prior to Sol-Gel	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24 hr	168 hr	336 hr	504 hr	672 hr	840 hr	
S 55-1 Alclad 2024 T3, 50-micron Alumina Grit Blasted	1.08	0.10	0.16	0,17	0.17	0.18	0.18	96% co
S 55-2 Alclad 2024 T3, MED Maroon Scotch-Brite™ Roloc™ Disc Abraded	1.08	0.06	0.13	0.13	0.16	0.16	0.16	94% co
S 55-3 Alclad 2024 T3, #220 Alumina Paper Abraded	0.96	0.14	0.18	0.18	0.18	0.20	0.20	98% co
S 55-4 Bare 2024 T3, #180 Alumina Grit Blasted	1.12	0.12	0.17	0.17	0.17	0.17	0.17	98% co
S 55-7 Bare 2024 T3, #220 Alumina Paper Abraded	1.16	0.14	0.21	0.21	0.23	0.23	0.23	97% co
S 55-8 Bare 2024 T3, #220 Alumina Paper Abraded, 30min @ 250°F Sol-Gel Coating Cure	1.24	0.13	0.22	0.22	0.26	0.28	0.28	86% co
S 55-9 Bare 2024 T3, 50-micron (#280) Alumina Grit Blasted	1.14	0.14	0.16	0.16	0.18	0.18	0.18	98% co

*co: cohesive failure within the adhesive layer

Table 2.4-20: Bare 2024-T3 Peel Test Results

Sample Number	Surface Preparation Method	Primer	Peel Test Method	Peel Test Temp	Dry or Water Sprayed	Peel Strength (pli)	Failure Mode (% co)
S 79-1	#180 Alumina Grit Blasted	BR 6747-1	Roller Peel	RT	Dry	84.1	75%
S 79-2	"	"	"	"	Water Sprayed	102.0	70%
S 79-3	"	"	"	-65°F	Dry	53.7	5%
S 79-4	"	"	Climbing Drum	RT	Dry	90.4	100%
S 79-5	"	"	"	-65°F	Dry	56.6	70%
S 79-6	#220 Alumina Sandpaper Sanded	BR 6747-1	Roller Peel	RT	Dry	86.6	90%
S 79-7	"	"	"	"	Water Sprayed	100.2	70%
S 79-8	"	"	"	-65°F	Dry	38.9	10%
S 79-9	"	"	Climbing Drum	RT	Dry	81.9	100%
S 79-10	"	"	"	-65°F	Dry	55.2	Mixed; 50%
S 87-1	MED Maroon Scotch-Brite™ Roloc™ Disc Abraded	BR 6747-1	Roller Peel	RT	Dry	85.9	100%
S 87-2	"	"	"	"	Water Sprayed	87.01	50%
S 87-3	"	"	"	-65°F	Dry	48.8	20%
S 87-4	"	"	Climbing Drum	RT	Dry	80.2	100%
S 87-5	"	"	"	-65°F	Dry	55.8	50%

Table 2.4-21: Alclad 2024-T3 Peel Test Results

Sample	Surface Prep.	Test Type and Conditions	Air-Dry Before Prime	Peel Strength (pli)	Failure Mode (% co)
S 91-1	#180 Alumina Grit Blasted	RT Dry Roller	180 Minutes	90.4	100%
S 91-2	"	RT Water Spray Roller	213 Minutes	82.4	Mixed; ~70%
S 91-3	"	-65°F Dry Roller	262 Minutes	77.2	Mixed; ~70%
S 91-4	"	RT Dry Climb. Drum	296 Minutes	70.5	100%
S 91-5	"	-65°F Dry Climb. Drum	320 Minutes	52.3	Mixed; ~70%
S 91-6	#220 Alumina Sanded	RT Dry Roller	180 Minutes	76.4	60%
S 91-7	"	RT Water Spray Roller	213 Minutes	66.0	40%
S 91-8	"	-65°F Dry Roller	262 Minutes	40.5	20%
S 91-9	"	RT Dry Climb. Drum	296 Minutes	81.5	100%
S 91-10	"	-65°F Dry Climb. Drum	320 Minutes	38.8	25%

2.5 Evaluation of Laser Deoxidation Process

Craig Walters Associates (CWA), Dublin OH, developed prototype lasers for an environmentally friendly alternative for paint stripping in aircraft applications[21]. It was also desired to demonstrate the feasibility of using lasers to deoxidize and "texturize" surfaces for adhesive bonding applications. The laser utilized by Craig Walters Associates was a Nd:YAG Big Sky Laser Technologies Model CFR 200-20. The wavelength of the pulses was 1064nm. Pulses were delivered through the fiber at 20Hz with pulse widths in the 15 to 25ns range and energy per pulse up to 200mJ. Two experiments were conducted over two separate trips to CWA. Boegel-EPII solution was used following laser deoxidation for preparation of the bonding surfaces. Wedge crack extension testing was performed to screen the process variables. Since the motorized table that supported the wedge test adherends was of limited size, 3.5-inch by 6-inch adherends were used for this experiment, yielding three 1-inch wide wedge test specimens per panel.

2.5.1 Laser Pretreatment Evaluation #1

CWA determined the laser settings for the first experiment. During that experiment, a nearly flat-top beam spatial profile was used. Two laser fluence levels were evaluated: a level intended for texturizing (1.4J/cm^2) and a level intended for texturizing and deoxidizing (2.5J/cm^2). Control data were generated via grit-blasting with 50-micron aluminum-oxide. Two surface preparations were evaluated after deoxidation: silane treatment followed by BR 127 primer as used in the grit-blast/silane (GBS) preparation and Boegel-EPII sol-gel solution followed by BR 6747-1 primer application. The purpose of using a silane treatment was to determine if using the laser to texturize a grit-blasted surface would improve the results in the wedge test when tested at 140°F and 95-100% RH. In past experiments, GBS performs well in wedge tests when conditioned at 120°F and 95-100% RH but fail when conditioned at 140°F and 94-100% RH[8].

Al 2024-T3 adherends were laser treated using one of the two fluence levels. Silane application for 10 minutes or Boegel-EPII solution application for 3 minutes followed. Silane-treated panels were dried at 200°F for 60 minutes prior to priming with BR 127. Boegel-EPII-treated adherends were dried for 30 minutes at ambient conditions (70°F and 60% RH) and primed with BR 6747-1. Both primers were spray applied and cured for 60 minutes at 250°F in an air-circulating oven. Treated adherends were bonded with 0.06psf AF 163-2M and cured for 60 minutes at 250°F under 35-40 psi in a portable autoclave. Specimens were tested at either120°F and 95-100% RH or 140°F and 95-100% RH. Control wedge test panels were fabricated using the optimized GBS surface preparation and grit-blast/Boegel-EPII process. GBS wedge test specimens were tested at 120°F and 95-100% RH in order to ensure the silane surface preparations were conducted correctly. Sol-gel wedge test specimens were tested at 140°F and 95-100% RH. Results of the control wedge test data are shown in Table 2.5-1. It should be noted that the GBS results (90% cohesive failure) are anomalous since these results are normally expected to be 100% cohesive after 28 days at 120°F and 95-100% RH[8].

Results using the laser to texturize the surface (1.4J/cm^2) are shown in Table 2.5-2. The specimens prepared with both the silane and Boegel-EPII processes exhibited adhesional (interfacial) failure modes. Results using the laser to texturize and deoxidize (2.5J/ cm^2) are shown in Table 2.5-3. Although the higher power setting used with Boegel-EPII improved performance in the wedge test, specimens still exhibited mostly interfacial failure. Further

investigation into the results determined that the bondlines of the laser-exposed specimens were much thinner than those of the control specimens. Table 2.5-4 displays the correlation between bondline thickness and failure mode. Specimens with bondlines thinner than 0.003 inch (3.0 mils) exhibited higher amounts of adhesional failure. The targeted bondline thickness was 0.005-inch (5.0 mils). Since bondlines were thin, another round of testing was required to generate data with acceptable bondline thicknesses.

Table 2.5-1: Control Wedge Test Data

Process	Test Condition	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
			1 hr	8 hr	24 hr	7 days	21 days	28 days	
Grit-blast / silane / BR 127	120°F & 95-100% RH	1.16	0.05	0.07	0.07	0.11	0.12	0.13	90% co
Grit-blast / Boegel EPII / BR 6747-1	140°F & 95-100% RH	1.13	0.03	0.07	0.10	0.17	0.22	0.24	95% co

* co: cohesive failure within the primer layer
Remaining noncohesive failure occured betweeen the primer and aluminum

Table 2.5-2: Effect of Using the Laser to Texturize (1.4J/cm^2) the Bonding Surface

Process	Test Condition	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
			1 hr	8 hr	24 hr	7 days	21 days	28 days	
Grit-blast/Laser/Silane/BR 127	140°F & 95-100% RH	1.30	0.06	0.14	0.17	0.25	0.32	0.32	20% co
Laser / Boegel EPII / BR 6747-1	140°F & 95-100% RH	1.24	0.13	0.19	0.25	0.36	0.47	0.51	0% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

Table 2.5-3: Effect of Using the Laser to Texturize and Deoxidize (2.5J/cm^2) Bonding Surface

Process	Test Condition	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
			1 hr	8 hr	24 hr	7 days	21 days	28 days	
Laser / Silane / BR 127	120°F & 95-100% RH	1.20	0.13	0.15	0.22	0.27	0.32	0.36	13% co
Laser / Boegel EPII / BR 6747-1	140°F & 95-100% RH	1.24	0.09	0.14	0.15	0.24	0.30	0.30	43% co

within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

Table 2.5-4: Comparison Between Bondline Thickness and Failure Mode

Deoxidation Process	Fluence (J/cm^2)	Surface Treatment	Bondline Thickness (mils)	Failure Mode
Grit-blast	n/a	GBS	4.6	90% co
Grit-blast	n/a	Boegel-EPII	4.6	95% co
Grit-blast / Laser	1.4	GBS	2.4	20% co
Laser	1.4	Boegel-EPII	2.4	0% co
Laser	2.5	GBS	2.1	13% co
Laser	2.5	Boegel-EPII	2.9	43% co

co: cohesive failure

2.5.2 Laser Pretreatment Evaluation #2

During the second laser experiment, two types of beam profiles were evaluated using Boegel-EPII: the flat-top profile used in the first experiment and a near-Gaussian profile. A concerted

effort was made to control bondline thickness to the target value of 5 mils. In an effort to improve the wedge test performance the BR 6747-1 primer was cocured with the adhesive. One set of specimens was fabricated using BR 6757-1 nonchromated bond primer. Several variables were evaluated in this second experiment: 1) laser profile; 2) alloy (Al 2024-T3 versus Al 7075-T6); 3) alloy cladding (clad versus bare); and 4) bond primer (BR 6747-1 versus BR 6757-1). Bondline thickness was successfully controlled to 5 mils $\pm$ 1 mil. All test panels were bonded with 0.06psf AF 163-2M and cured for 60 minutes at 250°F and 35-40 psi. Specimens were tested at 120°F and 95-100% RH. All results, shown in Table 2.5-5, appear to be much improved from the first experiment. Some improvement is likely due to better control over bondline thickness and cocuring of the bond primers with the adhesive. However, much is attributable to the 120°F rather than140°F conditioning temperature.

Table 2.5-5: Wedge Test Results for Laser Pretreatment Evaluation #2

Materials	Laser Profile	Initial (in)	Cummulative Crack Growth (in)						Failure Mode*
			1 hr	8 hr	24 hr	7 days	21 days	28 days	
Al 2024-T3 / BR 6747-1	n/a: grit-blast	1.09	0.01	0.09	0.09	0.13	0.16	0.17	98% co
Al 2024-T3 / BR 6747-1	Flat top	1.19	0.03	0.06	0.06	0.13	0.15	0.15	98% co
Al 2024-T3 / BR 6747-1	Gaussian	1.18	0.01	0.08	0.09	0.12	0.16	0.19	96% co
Al 2024-T3-clad / BR 6747-1	Flat top	1.09	0.01	0.12	0.14	0.16	0.18	0.18	95% co
Al 2024-T3-clad / BR 6747-1	Gaussian	1.15	0.03	0.09	0.12	0.14	0.15	0.17	97% co
Al 7075-T6 / BR 6747-1	Gaussian	1.21	0.02	0.09	0.11	0.11	0.13	0.13	80% co*
Al 2024-T3 / BR 6757-1	Gaussian	1.18	0.00	0.07	0.08	0.08	0.11	0.11	97% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

2.6 Evaluation of Solid State Cleaning and Deoxidation

Panels were fabricated according to the matrix in Table 2.6-1 to determine the feasibility of "solid-state" cleaning methods in conjunction with a sol-gel surface preparation. After cleaning, the panels were pretreated by grit-blasting or abrading (#220 alumina), treated with Boegel-EPII, and primed with BR 6747-1 (precured). The panels were all bonded with 3M AF 163-2M adhesive. Wedge test results for solid-state cleaned specimens and tankline controls are given in Table 2.6-2.

Table 2.6-1: Solid-State Cleaning Matrix

Specimen	Cleaning Method	Pretreatment	Surface Prep	Primer
B67-WG	wheat starch blast	grit-blasted	Boegel-EPII	Cytec BR 6747-1
B67-WS	wheat starch blast	abraded (#220 grit)	Boegel-EPII	Cytec BR 6747-1
B67-BG	wet sodium bicarbonate blast	grit-blasted	Boegel-EPII	Cytec BR 6747-1
B67-BS	wet sodium bicarbonate blast	abraded (#220 grit)	Boegel-EPII	Cytec BR 6747-1
B67-AG	Alconox	grit-blasted	Boegel-EPII	Cytec BR 6747-1
B67-AS	Alconox	abraded (#220 grit)	Boegel-EPII	Cytec BR 6747-1
B67-TG	tankline: Brulin 815GD, Turco® 2623 alkaline cleaners	grit-blasted	Boegel-EPII	Cytec BR 6747-1
B67-TS	tankline: Brulin 815GD, Turco® 2623 alkaline cleaners	abraded (#220 grit)	Boegel-EPII	Cytec BR 6747-1

Table 2.6-2: Wedge Test Performance for Solid-State Cleaning

Sample Number	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24hr	168hr	336hr	504hr	672hr	840hr	
B67-WG	1.26	0.11	0.13	0.13	0.13	0.13	0.13	97% co
B67-WS	1.19	0.16	0.26	0.29	0.30	0.30	0.30	30% co
B67-BG	1.24	0.11	0.15	0.15	0.15	0.15	0.15	98% co
B67-BS	1.25	0.18	0.33	0.42	0.43	0.48	0.49	0% co
B67-AG	1.22	0.10	0.13	0.14	0.14	0.14	0.14	99% co
B67-AS	1.18	0.18	0.24	0.26	0.26	0.29	0.29	60% co
B67-TG	1.18	0.11	0.15	0.15	0.15	0.15	0.15	98% co
B67-TS	1.18	0.17	0.26	0.31	0.31	0.32	0.32	70% co

*co: cohesive failure within the adhesive layer

From this testing, it is clear that surface cleaning changes manifest themselves more prominently in sanded specimens. All of the grit-blasted specimens in this series show better durability than the sanded analogs. The grit-blasted specimens resulted in >98% cohesive failure, while the sanded specimens failed in an adhesional manner (at the sol-gel-to-metal interface).

Use of Sponge-Jet™ hybrid media was attempted as a nonchemical method of cleaning, deoxidizing, and activating the surface of the metal for reaction with the sol-gel. There are many different types of Sponge-Jet™ media commercially available. For these studies, a moderately aggressive media that incorporates alumina particles within the sponge carrier was chosen. This media, designated Silver Sponge Media™, was recommended by the supplier for deoxidizing aluminum surfaces. The Sponge-Jet™ media (coarse) were loaded into a standard grit-blast chamber. The specimens were blasted using essentially the same blast parameters as with the alumina grit media. The wedge test results for this study are shown in Table 2.6-3. After blasting, there was inorganic media dust left on the surface of the aluminum panels. When this was removed using a compressed air blow or solvent wipe, the results were very good. However, if the media residues were removed with a water rinse, degradation in the hot/wet performance of the interface was seen presumably due to excessive hydrolyzation of the surface.

Table 2.6-3: Wedge Performance for Sponge-JetÔ Deoxidation

Sample Condition	Initial (in)	Cumulative Crack Growth (hrs)						Failure Mode*
		24	168	456	624	792	960	
Sponge-Jet™, Solvent Wipe	1.23	1.32	1.39	1.42	1.42	1.42	1.42	90% co
Sponge-Jet™, Water Rinse	1.26	1.38	1.47	1.56	1.56	1.56	1.56	70% co
Sponge-Jet™, Air Blow	1.23	1.31	1.40	1.40	1.40	1.41	1.41	94% co
Grit Blast, Air Blow	1.27	1.30	1.38	1.38	1.38	1.40	1.40	98% co

* co: cohesive failure within the adhesive layer
primer a little thick; some primer-to-adhesive interfacial failure

2.7 Evaluation of Water Jet Pretreatment Techniques

The National Defense Center for Environmental Excellence (NDCEE), operated by Concurrent Technologies Corporation (CTC), was tasked to evaluate water-jet processing for surface activation of aluminum and titanium prior to sol-gel application. As part of this task, two evaluations were completed. The first evaluation consisted of an initial round of processing/parameter development at CTC followed by wedge crack extension testing at the Air Force Research Laboratory (AFRL). Results of the initial processing were used to assess parameters for water-jet blasting so optimal parameters could be determined prior to the second evaluation. The second evaluation was used to verify the initial results as well as test additional parameters based on the Evaluation #1 data.

The adherends used in both evaluations consisted of bare Al 2024-T3, bare Al 7075-T6, and Ti-6Al-4V. All adherends were cleaned with acetone and wiped with lint-free wipes until no remaining trace of grease, dirt, or contamination was present prior to surface activation using an ultra-high pressure water jet (UHPWJ) process.

Surface activation of the adherends was accomplished using a United Technologies, Pratt & Whitney Water Jet Systems cell (Figure 2.7-1). The cell was composed of an Industrial Acoustics Company enclosure that housed a six-axis Fanuc S-420F robot that manipulated the high-pressure water rotary nozzle and a Koike Aronson Model RFT1.5SD turn table. The robot controlled the position of the turntable by utilizing a capability for a seventh axis.

A Jet Edge Model 55-150 intensifier pump supplied ultra-high pressure water in the range of 1 to 55,000 psi. Recirculated, treated water at 70 psi fed the Jet Edge pump. A Lamda WJ-1000C water reclamation unit received water from the work area, filtered out any entrained solids with a series of four filters ending in a 0.35 micron Harmsco filter, removed ions with a Culligan two-stage deionization system, adjusted the pH of the water with automated chemical additions, and then pumped the cleaned water to the Jet Edge pump. A volume of 300 gallons of water was used in this system. Deionized water was supplied as make-up to replace water lost through evaporation.

Figure 2.7-1: Pratt & Whitney Water Jet Systems Cell

The ultra-high pressure water was delivered to a United Technologies model 500T2028 eight-nozzle manifold (Figure 2.7-2) by way of an Applied Robotics tool adapter/exchange system fitted to the knuckle of the robot. The water stream from each nozzle was aligned at 90 degrees

to the manifold. By directing the robot, these streams could be positioned at any angle. Nozzles in sizes from 0.007 to 0.012 inch in diameter were arranged in the manifold so that an even pattern of water impinged on the work piece as the manifold was rotated at speeds of 500 rpm. Throughout processing, nozzles that had become plugged or flared were replaced with new nozzles. Due to limited parts availability, 0.007-inch diameter nozzles were, at times, replaced with 0.006-inch diameter nozzles.

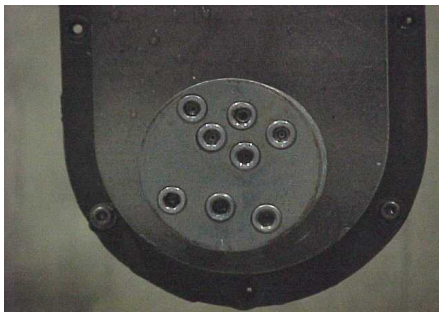


Figure 2.7-2: Model 500T2028 Eight-Nozzle Manifold

2.7.1 Water Jet Pretreatment Evaluation #1

The following five processing variables were evaluated in this program:

1. *Standoff distance*: distance between water jet nozzle and adherend
2. *Traverse rate*: speed that the nozzle moved across the adherend
3. *Blast angle*: angle between the nozzle and adherend
4. *Target pressure*: water pressure
5. *Number of passes*: number of passes the water jet made over a specific area

Several test standards were fabricated varying the above processing factors. These test standards were visually inspected and compared to a standard grit-blasted panel for similarities. A list of the different combinations of processing factors is shown in Table 2.7-1 along with a short description of the visual inspections. Based on the visual appearance of the panels after water jet blasting, parameter sets #9 and #16 were selected as being the most similar to a grit-blast surface on Al 2024-T3. Grit-blast and nylon-pad-abraded adherends were used as a control to ensure proper sol-gel application. Using parameter sets #9 and #16 as the baselines, additional parameter sets were selected that appeared to provide “lighter” and “heavier” abrasion than desired. This was done in order to determine how the sol-gel would perform with what appeared to be less and more aggressive surface blasting. The same procedure was then used to identify a baseline parameter set for use on Ti-6-4 adherends. These parameter sets were added to the grit-blast and nylon-pad controls to form the test matrix for Evaluation #1 processing using the sol-gel chemistry (Table 2.7-2).

The final matrix was processed twice to produce duplicate specimens of each parameter set selected for testing. In all, fifty-two (52) adherends were processed, for a total of twenty-six (26) wedge test panels.

Table 2.7-1: Evaluated Water Jet Processing Parameters

Set #	Substrate	Stand-Off Distance (in)	Traverse Rate (in/s)	Blast Angle (°)	Target Pressure (ksi)	No. of Passes	Comments
1	2024-T3	4	0.4	90	45	1	Profile too light.
2	2024-T3	4	0.4	90	35	1	Profile too light.
3	2024-T3	4	0.24	90	35	1	Profile very light. Slightly grooved surface.
4	2024-T3	4	0.08	90	35	1	Grooved surface.
5	2024-T3	3	0.4	90	35	1	Profile very light. Uneven pattern.
6	2024-T3	3	0.4	90	45	1	Uneven pattern.
7	2024-T3	4	0.4	90	40	1	Profile very light. Uneven pattern.
8	2024-T3	4	0.4 / 0.8	90	45	2	Smooth and even surface.
9	2024-T3	4	0.4	90	45	2	Even surface. More grooved then #8.
10	2024-T3	4	0.8 / 0.4	90	45	2	Profile lighter & more patterned than #8.
11	2024-T3	4	0.8 / 0.4	90	45	2	Profile lighter & more patterned then #8.
12	2024-T3	4	0.4	45	45	2	Lighter profile than same parameters with 90° angle.
13	2024-T3	4	0.4	45	55	2	Same as #12 – only achieved 47 ksi pressure.
14	2024-T3	3	0.4	45	45	2	Good surface. Lighter than #9 & streaked.
15	2024-T3	3	0.4	45	55	2	Good surface. Heavier than #9 with grooves.
16	2024-T3	4	0.4	45	55	2	Smooth and even surface.
17	7075-T6	4	0.4	45	55	2	Profile too light.
18	7075-T6	4	0.4	45	55	3	Grooved surface.
19	7075-T6	3	0.4	45	55	2	Smooth and even surface.
20	Ti-6Al-4V	3	0.24	45	55	2	Profile too light.
21	Ti-6Al-4V	2	0.4	90	55	3	Good surface. Profile a little light – try extra passes when processing.
22	Ti-6Al-4V	1	0.4	90	55	3	Surface patterned and grooved.
23	2024-T3	4	0.4	90	35 / 45	2	Very light and patterned surface.
24	2024-T3	4	0.24	90	35	2	Light and patterned surface. Slightly more aggressive than #23.

Table 2.7-2: Water Jet Evaluation #1 Test Matrix

Panel ID	Standoff Distance (in)	Traverse Rate (in/s)	Blast Angle (°)	Target Pressure (ksi)	No. of Passes
Al 2024-T3 Grit-Blast Control	N/A	N/A	N/A	N/A	N/A
Ti-6Al-4V Grit-Blast Control	N/A	N/A	N/A	N/A	N/A
Al 2024-T3 Baseline #1: Set #9	4	0.4	90	45	2
Al 2024-T3 Very Light Scenario: Set #6	3	0.4	90	45	1
Ti-6Al-4V Baseline: Set #21	2	0.4	90	55	3
Ti-6Al-4V Heavy Scenario: Set – N/A	2	0.4	90	55	4
Ti-6Al-4V Very Heavy Scenario: Set – N/A	2	0.4	90	55	5
Ti-6Al-4V Cocures: Very Heavy Set	2	0.4	90	55	5
Al 2024-T3 Baseline #2: Set #16	4	0.4	45	55	2
Al 2024-T3 Cocures: Set #16	4	0.4	45	55	2
Al 2024-T3 Heavy Scenario: Set #15	3	0.4	45	55	2
Al 2024-T3 Light Scenario: Set #14	3	0.4	45	45	2
Al 2024-T3: Nylon Pad Cocures	N/A	N/A	N/A	N/A	N/A

After deoxidation, sol-gel was brush applied within 3 to 40 minutes to the water-jet-activated adherends, grit-blast controls, and nylon-pad-abraded controls using an acid-free natural bristle brush. The surface of the adherends was kept continuously wet with the sol-gel solution for 3 minutes and then allowed to air-dry at room temperature for a minimum of 30 minutes. Sol-gel treated adherends were primed using BR 6747-1. The adherends were allowed to air-dry at room temperature for 30 minutes and cured at 250°F for one hour prior to adhesive application. The primer on the cocure adherends was allowed to air-dry at room temperature prior to adhesive application and cure in a single cure cycle. All wedge tests were performed at 140°F and 98% RH. Results of the testing performed in Evaluation #1 are shown in Table 2.7-3. Two sets of data are shown for each set of parameters.

The crack growths after 28 days of exposure for the Al 2024-T3 specimens prepared using water-jet surface activation ranged from 0.11 to 0.19 inch. These values are consistent with the crack growths exhibited by the grit-blast (0.20-0.24 inch) and the Scotch-Brite™ (0.20-0.29 inch) controls. While all Al 2024-T3 specimens prepared using water-jet surface activation exhibited similar crack growth to the control panels, not all panels exhibited cohesive failure modes. Results for specimens prepared using parameter sets #15 (Heavy Scenario) and #16 (Baseline #2) ranged from 75 to 86% cohesive failure, all well below the desired 95-100% cohesive value. However, results for specimens prepared using parameter sets #6 (Very Light Scenario), #9 (Baseline #1), and #14 (Light Scenario) were 94 and 99%, 95 and 89%, and 99 and 80%, respectively. Although only one of the duplicate samples for a given set of parameters met the established requirement, results were promising enough to warrant inclusion of these parameter sets in Evaluation #2 testing.

All Evaluation #1 titanium Ti-6-4 specimens prepared using water-jet surface activation exhibited acceptable crack growths after 28 days of exposure with values ranging from 0.17 to 0.33 inches. However, all titanium samples, including the grit blast controls, did not exhibit cohesive failure modes, with values ranging from 0 to 84% cohesive failure. EDX analysis was used to determine that the failure mode for these samples seemed to occur at the primer to metal interface, evidenced by a lack of chromium on the adhesive. Failure of this type is normally indicative of a problem with the primer. However, since the aluminum specimens did not exhibit the same failure mode, it is not believed that the primer was at fault in this case. It was unclear what caused the failure of the titanium specimens.

2.7.2 Water Jet Pretreatment Evaluation #2

Parameter sets #6, #9, and #14 were selected for the Al 2024-T3 testing in Evaluation #2 based on the results of the Evaluation #1 testing. These parameter sets showed the most promising results, with failure modes generally above 90% cohesive failure in the adhesive. Since the results of the light scenario (parameter set #14) appeared to be promising, parameter set #5 (very, very light scenario) was also added to the matrix to determine if an even less aggressive surface blast would provide good results. Only the baseline parameter set (three passes) and the heavy scenario parameter set (four passes) were re-evaluated for Ti-6Al-4V testing in Evaluation #2.

In addition to 2024-T3 and titanium, two other adherends were added to the matrix for Evaluation #2. First, Al 7075-T6 was added in order to determine if the water-jet surface activation parameters selected for use on Al 2024-T3 would be effective on due to differences in

hardness. Second,
Al 2024-T3 adherends contaminated with Release-All #100 (Airtech International, Inc.) were added to the matrix. Release-All #100 is a release agent that would likely cause gross failures in the wedge test if not completely removed from the adherend surfaces prior to bonding. Panels contaminated with Release-All #100 were not cleaned with acetone prior to water-jet surface activation. Therefore, the water jet was used not only to activate the surface, but also to clean it; thereby eliminating the solvent-cleaning step currently used.

Table 2.7-3: Water Jet Evaluation #1 Wedge Test Results (140°F & 98% RH)

Panel ID	Stand-Off Distance (in)	Traverse Rate (in/s)	Blast Angle (°)	Target Pressure (ksi)	No. of Passes	Bondline Thickness (in)	Crack Growth After 28 Days Exposure (in)	Failure Mode
Al 2024-T3 Grit-Blast Control	N/A	N/A	N/A	N/A	N/A	0.0040	0.24	89%*
						0.0034	0.20	95% co
Al 2024-T3 Nylon Pad Cocures	N/A	N/A	N/A	N/A	N/A	0.0037	0.29	92% co
						0.0044	0.20	95% co
Al 2024-T3 Baseline #1: Set #9	4	0.4	90	45	2	0.0051	0.13	95% co
						0.0050	0.16	89% co
Al 2024-T3 Very Light: Set #6	3	0.4	90	45	1	0.0041	0.19	94% co
						0.0048	0.17	99% co
Al 2024-T3 Baseline #2: Set #16	4	0.4	45	55	2	0.0050	0.14	78% co
						0.0041	0.17	75% co
Al 2024-T3 Cocures: Set #16	4	0.4	45	55	2	0.0067	0.17	84% co
						0.0052	0.19	78% co
Al 2024-T3 Heavy Scenario: Set #15	3	0.4	45	55	2	0.0025	0.16	86% co
						0.0032	0.11	84% co
Al 2024-T3 Light Scenario: Set #14	3	0.4	45	45	2	0.0035	0.14	99% co
						0.0030	0.12	80% co
Ti-6Al-4V Grit-Blast Control	N/A	N/A	N/A	N/A	N/A	0.0069	0.18	69% co
						0.0057	0.18	45% co
Ti-6Al-4V Baseline: Set #21	2	0.4	90	55	3	0.0062	0.22	43% co
						0.0059	0.19	41% co
Ti-6Al-4V Heavy Scenario: Set–N/A	2	0.4	90	55	4	0.0060	0.15	68% co
						0.0051	0.21	0% co
Ti-6Al-4V Very Heavy Scenario: Set N/A	2	0.4	90	55	5	0.0061	0.17	84% co
						0.0062	0.19	30% co
Ti-6Al-4V Cocures: Very Heavy Parameter Set	2	0.4	90	55	5	0.0067	0.18	53% co
						0.0058	0.33	0% co

* Failure occurred between primer and adhesive
co: cohesive failure within the adhesive layer

As with Evaluation #1, grit-blast and nylon-pad controls were added to form the complete matrix for Evaluation #2 processing using the sol-gel chemistry (Table 2.7-4). The complete matrix was processed twice to produce duplicate specimens of each parameter set selected for testing. Fifty-two adherends were processed, for a total of twenty-six (26) wedge test specimens.

Results of Evaluation #2 Testing is shown in Table 2.7-5. Two sets of data are shown for each set of parameters. The crack growths after 28 days of exposure for the Al 2024-T3 specimens prepared using water-jet surface activation ranged from 0.14 to 0.39 inch. Most of the specimens

exhibited crack growths consistent with the crack growths exhibited by the grit-blast controls (0.22-0.28 inch). In addition, the water-jet blasted samples performed as good as or better than the nylon-pad (0.36-0.38 inch) controls. Failure mode results for specimens prepared using parameter set 5 (Very, Very Light Scenario) clearly did not meet the requirements with values of 38 and 69% cohesive failure. However, failure mode analysis of the remaining samples showed mixed results. As in Evaluation #1, specimens prepared using parameter sets #6 (Very Light Scenario) and #9 (Baseline #1) each had one sample that met or exceeded the 95% cohesive failure requirement and one that did not. Both samples prepared using parameter set #14 (Light Scenario) failed to meet the requirement, however, both the precured and cocured samples had one specimen with 93% cohesive failure. In addition, the water jet process appeared to satisfactorily remove the Release-All #100 contaminant from the aluminum surface. Although the results were not as consistent as desired, the water jet process showed enough promise to warrant future work by any organization that has a water jet and interest in sol-gel prebond surface preparation.

Table 2.7-4: Water Jet Evaluation #2 Sol-Gel Processing Matrix

Panel ID	**Standoff Distance (in)**	**Traverse Rate (in/s)**	**Blast Angle (°)**	**Target Pressure (ksi)**	**No. of Passes**
Al 2024-T3 Grit-Blast Control	N/A	N/A	N/A	N/A	N/A
Ti-6Al-4V Grit-Blast Control	N/A	N/A	N/A	N/A	N/A
Al 2024-T3 Very Light Scenario Parameter Set #6	3	0.4	90	45	1
Al 2024-T3 Very Light Scenario Cocures Parameter Set #6	3	0.4	90	45	1
Al 2024-T3 Very Light Scenario Release-All #100	3	0.4	90	45	1
Al 2024-T3 Light Scenario Parameter Set #14	3	0.4	45	45	2
Al 2024-T3 Light Scenario Cocures Parameter Set #14	3	0.4	45	45	2
Al 2024-T3 Very, Very Light Scenario Parameter Set #5	3	0.4	90	35	1
Al 2024-T3 Baseline #1 Parameter Set #9	4	0.4	90	45	2
Al 7075-T6 Baseline Parameter Set #19	3	0.4	45	55	2
Ti-6Al-4V Baseline Parameter Set #21	2	0.4	90	55	3
Ti-6Al-4V Heavy Scenario Parameter Set – N/A	2	0.4	90	55	4
Al 2024-T3 Scotch-Brite™ Cocures	N/A	N/A	N/A	N/A	N/A

Table 2.7-5: Water Jet Evaluation #2 Wedge Test Results (140°F & 98% RH)

Panel ID	Stand-Off Distance (in)	Traverse Rate (in/s)	Blast Angle (°)	Target Pressure (ksi)	No. of Passes	Glue Line Thickness (in)	Crack Growth After 28 Days Exposure (in)	Failure Mode(1)
2024-T3 Grit-Blast Control	N/A	N/A	N/A	N/A	N/A	0.0041	0.28	99% co
						0.0044	0.22	100% co
2024-T3 Scotch-Brite™ Cocures	N/A	N/A	N/A	N/A	N/A	0.0031	0.36	46%(2)
						0.0034	0.38	58%(2)
2024-T3 Very Light Scenario Parameter Set #6	3	0.4	90	45	1	0.0030	0.26	91% co
						0.0050	0.22	95% co
2024-T3 Cocures Very Light Scenario Parameter Set #6	3	0.4	90	45	1	0.0040	0.23	87% co
						0.0041	0.14	94% co
2024-T3 Release-All #100 Very Light Scenario Parameter Set #6	3	0.4	90	45	1	0.0057	0.27	99% co
						0.0050	0.19	99% co
2024-T3 Light Scenario Parameter Set #14	3	0.4	45	45	2	0.0034	0.27	38%(3)
						0.0039	0.16	93% co
2024-T3 Cocures Light Scenario Parameter Set #14	3	0.4	45	45	2	0.0044	0.35	22%(2)
						0.0048	0.19	93% co
2024-T3 Very, Very Light Scenario Parameter Set #5	3	0.4	90	35	1	0.0027	0.39	38%(2)
						0.0042	0.25	69% co
2024-T3 Baseline #1 Parameter Set #9	4	0.4	90	45	2	0.0030	0.17	84% co
						0.0042	0.24	95% co
7075-T6 Baseline Parameter Set #19	3	0.4	45	55	2	0.0044	0.32	28%(3)
						0.0043	0.34	40%(2)
						0.0058	0.27	48%(2)
Ti-6Al-4V Grit-Blast Control	N/A	N/A	N/A	N/A	N/A	0.0043	0.30	32%(2)
						0.0045	0.19	66%(2)
Ti-6Al-4V Baseline Parameter Set #21	2	0.4	90	55	3	0.0052	0.22	66%(2)
						0.0061	0.23	62%(2)
Ti-6Al-4V Heavy Scenario Parameter Set – N/A	2	0.4	90	55	4	0.0056	0.26	58%(2)
						0.0056	0.20	79%(2)

(1) "co" indicates that the failure was cohesive in the adhesive layer.
(2) Failure was at the primer-to-metal interface.
(3) Failure was in the primer layer.

2.8 Nonchromated Process Film Adhesive Study

Field-level use of bond primers is often difficult and impractical due to the limited equipment and time restraints. Therefore, an evaluation was conducted to determine the effect of using sol-gel surface preparations without bond primer in conjunction with epoxy film adhesives requiring elevated temperature cure cycles. The PAA controls were primed and were expected to outperform the scuff/wipe controls and the unprimed sol-gel processes. Five different adhesives were evaluated in this study:

- Cytec FM 73, 0.085psf, knit carrier

- Cytec FM 73M, 0.06psf, mat carrier
- 3M Company AF 163-2M, 0.06psf, mat carrier
- Loctite's Hysol EA 9628, 0.06psf, mat carrier
- Loctite's Hysol EA 9696, 0.06psf, mat carrier.

Al 2024-T3 adherends were treated with PAA/BR 127, PAA/BR 6747-1, grit-blast/sol-gel, nylon-pad/sol-gel, or scuff-sand/solvent wipe surface preparations with acetone as the solvent. Adherends were bonded with the appropriate adhesives and cured in a zip-vac for 60 minutes at 250°F and 15in Hg. Vacuum pressure was used to mimic field-level processing conditions. The test matrix for this no-prime film adhesive study is shown in Table 2.8-1. The matrix was repeated for each film adhesive.

Table 2.8-1: Nonchromated Process Film Adhesive Test Matrix

Surface Prep	Number of Specimens per Condition					
	Lap Shear				Peel	Wedge Test
	RT (70°F)	160°F	180°F	180°F wet*	RT (70°F)	120°F & 95-100% RH
PAA/BR 127	5	5	5	5	5	5
PAA/BR 6747-1	5	5	5	5	5	5
Scuff-sand/Solvent wipe	5	5	5	5	5	5
Grit-blast/Sol-gel/No primer	5	5	5	5	5	5
Nylon-pad/Sol-gel/No primer	5	5	5	5	5	5

*wet lap shear testing consists of aging machined specimens for 60 days at 140°F & 95% RH prior to mechanical testing at 180°F.

2.8.1 Cytec FM 73 (0.085psf)

Results of the FM 73 lap shear and floating roller peel testing are shown in Table 2.8-2. Sol-gel lap shear specimens exhibited mixed failure modes and slight reductions in bond strengths when compared to PAA specimens. Hot/wet sol-gel lap shear specimens exhibited complete adhesional failure. All scuff-sand/solvent wipe specimens exhibited adhesional failure. All peel specimens failed cohesively except the scuff-sand/solvent wipe specimens.

Results for the FM 73 (0.085psf) wedge tests are shown in Table 2.8-3. Only the PAA specimens failed cohesively. However, the sol-gel specimens exhibited much better resistance to crack growth than scuff-sand/solvent wipe specimens.

Table 2.8-2: FM 73 (0.085psf) Lap Shear and Floating Roller Peel Test Results

Surface Preparation	Average of 5 Specimens (Failure Mode)				
	Lap Shear (psi)				Peel (pli)
	RT	160°F	180°F	180°F wet	RT
PAA/BR 127	6196 (90% co)	4486 (84% co)	3566 (76% co)	2317 (80% co)	89.4 (100% co)
PAA/BR 6747-1	6105 (93% co)	4224 (89% co)	4049 (80% co)	2389 (76% co)	94.8 (100% co)
Scuff-sand/Solvent wipe	4841 (30% co)	2790 (7% co)	2433 (-0-% co)	520 (-0-% co)	42.9 (-0-% co)
Grit-blast/Sol-gel/No primer	5299 (54% co)	4065 (12% co)	3632 (10% co)	1682 (-0-% co)	87.4 (100% co)
Nylon-pad/Sol-gel/No primer	5333 (60% co)	4001 (36% co)	4011 (18% co)	1456 (3% co)	75.0 (95% co)

co: cohesive failure within the adhesive layer

Table 2.8-3: FM 73 (0.085psf) Wedge Test (120°F & 98% RH) Results

Surface Preparation	Initial (inches)	Cumulative Crack Growth (inches)							Failure Mode*
		1 hour	8 hours	24 hours	7 days	14 days	21 days	28 days	
PAA/BR 127	1.08	0.00	0.00	0.03	0.03	0.03	0.03	0.03	100% co
PAA/BR 6747-1	1.00	0.04	0.04	0.05	0.05	0.05	0.05	0.05	100% co
Scuff-sand/Solvent wipe	1.35	2.38	2.69	2.85	2.92	2.93	2.93	3.02	-0-% co
Grit-blast/Sol-gel/No primer	1.10	0.07	0.10	0.14	0.18	0.22	0.25	0.28	42% co
Nylon-pad/Sol-gel/No primer	1.07	0.08	0.22	0.41	0.68	0.66	0.75	0.77	-0-% co

* co: cohesive failure within the adhesive layer

2.8.2 Cytec FM 73M (0.06psf)

Results of the FM 73M lap shear and floating roller peel testing are shown in Table 2.8-4. Sol-gel lap shear specimens tested at RT exhibited cohesive failures. However, sol-gel lap shear specimens tested at elevated temperature exhibited mixed failure modes and slight reductions in bond strengths when compared to PAA specimens. Hot/wet sol-gel lap shear specimens exhibited complete adhesional failure. All scuff-sand/solvent wipe specimens exhibited adhesional failure and reduced bond strengths. The scuff-sand/solvent wipe specimens tested at 180°F after 60 days exposure to 140°F and 98% RH fell apart after removal from the exposure chamber and prior to testing. All peel specimens failed cohesively except the scuff-sand/solvent wipe specimens.

Table 2.8-4: FM 73M (0.06psf) Lap Shear and Floating Roller Peel Test Results

Surface Preparation	Average of 5 Specimens (Failure Mode)				
	Lap Shear (psi)				Peel (pli)
	RT	160°F	180°F	180°F wet	RT
PAA/BR 127	5859 (100% co)	4138 (100% co)	4161 (98% co)	2223 (90% co)	73.0 (100% co)
PAA/BR 6747-1	5804 (100% co)	4032 (98% co)	4363 (96% co)	2693 (82% co)	70.2 (100% co)
Scuff-sand/Solvent wipe	3283 (40% co)	2487 (13% co)	2080 (6% co)	-0- (0% co)	17.9 (-0-% co)
Grit-blast/Sol-gel/No primer	5317 (100% co)	3452 (95% co)	3480 (68% co)	1523 (-0-% co)	63.6 (100% co)
Nylon-pad/Sol-gel/No primer	5237 (95% co)	3618 (66% co)	3125 (60% co)	1083 (-0-% co)	61.0 (100% co)

co: cohesive failure within the adhesive layer

Results for the FM 73M (0.06psf) wedge tests are shown in Table 2.8-5. Only the PAA specimens failed cohesively. However, the sol-gel specimens exhibited much better resistance to crack growth than scuff-sand/solvent wipe specimens. Scuff-sand/solvent wipe specimens resulted in complete adhesional failures and exhibited an average crack growth of more than 4 inches at the 1-hour reading.

Table 2.8-5: FM 73M Wedge Test (120°F & 98% RH) Results

Surface Preparation	Initial (inches)	Cumulative Crack Growth (inches)							Failure Mode*
		1 hour	8 hours	24 hours	7 days	14 days	21 days	28 days	
PAA/BR 127	1.33	0.00	0.01	0.01	0.01	0.02	0.02	0.03	100% co
PAA/BR 6747-1	1.24	0.01	0.01	0.02	0.02	0.06	0.06	0.06	100% co
Scuff-sand/Solvent wipe	1.63	4.00+	Removed due to excessive crack length.						-0-% co
Grit-blast/Sol-gel/No primer	1.29	0.09	0.10	0.13	0.20	0.29	0.31	0.34	24% co
Nylon-pad/Sol-gel/No primer	1.28	0.04	0.06	0.09	0.25	0.49	0.53	0.56	2% co

* co: cohesive failure within the adhesive layer

2.8.3 3M Company AF 163-2M (0.06psf)

Results of the AF 163-2M lap shear and floating roller peel testing are shown in Table 2.8-6. Sol-gel lap shear specimens exhibited mixed failure modes and slight reductions in bond strengths when compared to PAA specimens. Hot/wet sol-gel lap shear specimens exhibited complete adhesional failure. Scuff-sand/solvent wipe specimens exhibited mainly cohesive failure modes when tested dry but complete interfacial failure when tested hot/wet. All peel specimens failed cohesively except the scuff-sand/solvent wipe specimens.

Table 2.8-6: AF 163-2M Lap Shear and Floating Roller Peel Test Results

Surface Preparation	Average of 5 Specimens (Failure Mode)				
	Lap Shear (psi)				Peel (pli)
	RT	160°F	180°F	180°F wet	RT
PAA/BR 127	4952 (95% co)	3542 (85% co)	3039 (80% co)	2076 (95% co)	73.4 (100% co)
PAA/BR 6747-1	5712 (95% co)	3604 (95% co)	3196 (95% co)	1957 (90% co)	72.4 (100% co)
Solvent	3969 (95% co)	3309 (90% co)	2826 (90% co)	1204 (-0-% co)	51.2 (12% co)
Grit-blast/Sol-gel/No primer	3674 (80% co)	2515 (70% co)	2299 (50% co)	1040 (5% co)	64.9 (100% co)
Nylon-pad/Sol-gel/No primer	4743 (80% co)	3186 (70% co)	2515 (40% co)	1108 (-0-% co)	66.8 (100% co)

co: cohesive failure within the adhesive layer

Results for the FM 73M (0.06psf) wedge tests are shown in Table 2.8-7. Only the PAA specimens and grit-blast/sol-gel specimens failed cohesively. Both grit-blast and nylon-pad/sol-gel specimens exhibited much better resistance to crack growth than scuff-sand/solvent wipe specimens. Scuff-sand/solvent wipe specimens exhibited an average crack growth of approximately 1 inch after 7 days exposure ands failures that were completely adhesional.

Table 2.8-7: AF 163-2M Wedge Test (120°F & 98% RH) Results

Surface Preparation	Initial	Cumulative Crack Growth (inches)							Failure
	(inches)	1 hour	8 hours	24 hours	7 days	14 days	21 days	28 days	Mode*
PAA/BR 127	1.20	0.03	0.05	0.07	0.08	0.10	0.12	0.12	99% co
PAA/BR 6747-1	1.12	0.05	0.05	0.06	0.09	0.10	0.10	0.10	94% co
Scuff-sand/Solvent wipe	1.30	0.33	0.39	0.63	0.99	1.13	1.16	1.16	-0-% co
Grit-blast/Sol-gel/No primer	1.19	0.10	0.11	0.15	0.19	0.20	0.21	0.22	98% co
Nylon-pad/Sol-gel/No primer	1.09	0.08	0.09	0.13	0.21	0.23	0.25	0.30	41% co

* co: cohesive failure within the adhesive layer

2.8.4 Loctite Hysol EA 9628 (0.06psf)

Results of the EA 9628 lap shear and floating roller peel testing are shown in Table 2.8-8. Sol-gel lap shear specimens exhibited mixed failure modes and slight reductions in bond strengths when compared to PAA specimens. Hot/wet sol-gel lap shear specimens exhibited complete adhesional failure. Scuff-sand/solvent wipe lap shear specimens exhibited adhesional failure modes. All peel specimens failed cohesively except the scuff-sand/solvent wipe specimens.

Results for the EA 9628 wedge tests are shown in Table 2.8-9. Both PAA and sol-gel treated specimens failed cohesively. Scuff-sand/solvent wipe specimens exhibited an average crack growth of more than 3 inches by the 1-hour reading with complete adhesional failures.

Table 2.8-8: EA 9628 Lap Shear and Floating Roller Peel Test Results

Surface Preparation	Average of 5 Specimens (Failure Mode)				
	Lap Shear (psi)				Peel (pli)
	RT	160°F	180°F	180°F wet	RT
PAA/BR 127	5726 (100% co)	4909 (97% co)	4600 (98% co)	3288 (85% co)	51.5 (100% co)
PAA/BR 6747-1	5846 (100% co)	5036 (97% co)	4461 (96% co)	3849 (100% co)	59.8 (100% co)
Solvent	5247 (34% co)	4019 (-0-% co)	3172 (-0-% co)	1580 (-0-% co)	19.2 (-0-% co)
Grit-blast/Sol-gel/No primer	4588 (85% co)	3719 (80% co)	3553 (60% co)	2093 (-0-% co)	53.2 (100% co)
Nylon-pad/Sol-gel/No primer	5129 (46% co)	4233 (28% co)	3934 (16% co)	2440 (-0-% co)	54.0 (100% co)

co: cohesive failure within the adhesive layer

Table 2.8-9: EA 9628 Wedge Test (120°F & 98% RH) Results

Surface Preparation	Initial (inches)	Cumulative Crack Growth							Failure Mode*
		1 hour	8 hours	24 hours	7 days	14 days	21 days	28 days	
PAA/BR 127	1.28	0.02	0.02	0.04	0.04	0.04	0.04	0.05	100% co
PAA/BR 6747-1	1.38	0.03	0.05	0.06	0.06	0.06	0.06	0.06	100% co
Scuff-sand/Solvent wipe	2.11	3.27	Removed due to excessive crack length.						-0-% coh
Grit-blast/Sol-gel/No primer	1.48	0.05	0.05	0.08	0.10	0.10	0.10	0.10	99% co
Nylon-pad/Sol-gel/No primer	1.33	0.04	0.06	0.13	0.15	0.16	0.16	0.16	98% co

* co: cohesive failure within the adhesive layer

2.8.5 Loctite Hysol EA 9696 (0.06psf)

Results of the EA 9696 lap shear and floating roller peel testing are shown in Table 2.8-10. Sol-gel lap shear specimens exhibited mostly cohesive failure modes and slight reductions in bond strengths when compared to PAA specimens. Hot/wet sol-gel lap shear specimens exhibited adhesional failure. Scuff-sand/solvent wipe lap shear specimens exhibited adhesional failure modes. All peel specimens failed cohesively except the scuff-sand/solvent wipe specimens.

Table 2.8-10: EA 9696 Lap Shear and Floating Roller Peel Test Results

Surface Preparation	Average of 5 Specimens (Failure Mode)				
	Lap Shear (psi)				Peel (pli)
	RT	160°F	180°F	180°F wet	RT
PAA/BR 127	4935 (95% co)	4176 (90% co)	4366 (95% co)	1765 (96% co)	73.0 (100% co)
PAA/BR 6747-1	5487 (95% co)	4932 (95% co)	4446 (95% co)	2358 (87% co)	70.2 (100% co)
Scuff-sand/Solvent wipe	5152 (63% co)	3658 (-0-% co)	3316 (-0-% co)	1058 (-0-% co)	17.9 (-0-% co)
Grit-blast/Sol-gel/No primer	4427 (90% co)	3763 (90% co)	3453 (90% co)	1834 (10% co)	63.6 (100% co)
Nylon-pad/Sol-gel/No primer	5290 (95% co)	4226 (90% co)	3612 (70% co)	1765 (5% co)	61.0 (100% co)

co: cohesive failure within the adhesive layer

Results for the EA 9696 wedge testing are shown in Table 2.8-11. Both PAA and sol-gel specimens failed cohesively. Scuff-sand/solvent wipe specimens exhibited an average crack growth of approximately 2 inches by the 1-hour reading with complete adhesional failures.

Table 2.8-11: EA 9696 Wedge Test (120°F & 98% RH) Results

Surface Preparation	Initial (inches)	Cumulative Crack Growth (inches)							Failure Mode*
		1 hour	8 hours	24 hours	7 days	14 days	21 days	28 days	
PAA/BR 127	1.30	0.06	0.06	0.06	0.07	0.07	0.07	0.07	100% co
PAA/BR 6747-1	1.33	0.02	0.02	0.03	0.06	0.06	0.06	0.06	100% co
Scuff-sand/Solvent wipe	1.35	1.93	1.98	2.30	2.91	3.03	3.14	3.14	-0-% co
Grit-blast/Sol-gel/No primer	1.23	0.06	0.06	0.08	0.09	0.09	0.13	0.13	100% co
Nylon-pad/Sol-gel/No primer	1.27	0.03	0.03	0.07	0.09	0.15	0.17	0.18	99% co

* co: cohesive failure within the adhesive layer

2.8.6 Summary of Film Adhesive No-prime Evaluation

In order to estimate the overall effect of surface preparation for each adhesive, a chart comparing the average percent cohesive failure for all lap shear, peel, and wedge test specimens for each surface preparation process is shown in Figure 2.8-1. This was a qualitative comparison based solely on failure modes. Since it includes lap shear, peel, and wedge test data, it is possible that one test, such as the wedge test, can have a large influence on the results. The PAA processes with both bond primers yielded the highest average amount of cohesive failure for each adhesive. This process was also the only one that included adhesive bond primer. The nylon-pad/sol-gel process yielded a higher average amount of cohesive failure than the scuff-sand/solvent wipe process for every adhesive. For all adhesives tested, the sol-gel processes provided reduced amounts of cohesive failure when compared to PAA/primer. However, when using EA 9696, the sol-gel (no primer) processes yielded an average of 91-94% cohesive failure mode, when compared to the 97% cohesive mode routinely achieved with PAA/primer. This was the best failure mode achieved using the sol-gel processes with any of the film adhesives. It should also be noted that sol-gel specimens bonded with EA 9628 and EA 9696 exhibited cohesive failures after 28 days exposure to 120°F and 98% RH, even without the use of a bond primer in the process. However, there was a significant drop in lap shear strength and percentage of cohesive failure mode for sol-gel specimens tested at 180°F after 60 days exposure to 140°F and 98% RH. This result is not completely understood and will require further evaluation. Scuff-sand/solvent wipe specimens exhibited very low percentages of cohesive failure and reduced strengths.

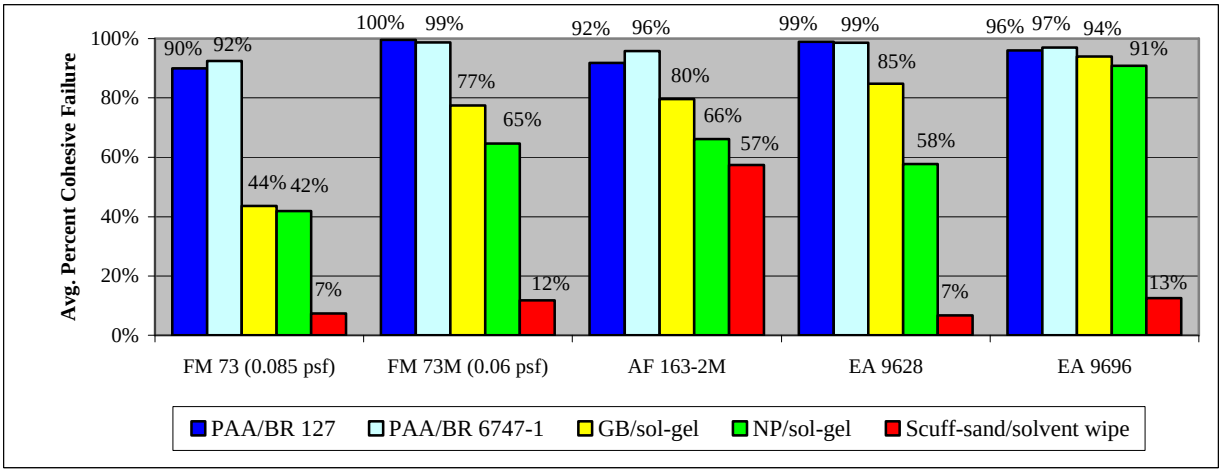


Figure 2.8-1: Average Percent Cohesive Failure versus Surface Preparation for Various Film Adhesives

2.9 Nonchromated Low-Temperature Two-Part Paste Adhesive Study

This evaluation of ambient-temperature adhesive bonding processes included a determination of initial paste adhesive strengths as well as an investigation into the effect of surface preparation on bond strength and moisture durability[22]. The two-part epoxy paste adhesives evaluated in the program included Hysol EA 9309.3NA, Hysol EA 9320NA, Hysol EA 9330.3, Hysol EA 9394, and Hysol EA 9396 from Henkel Loctite as well as 3M Company EC-2615 and EC-3333. Initial strengths were determined via tensile lap shear and floating roller peel testing using Al 2024-T3 adherends prepared with PAA and Cytec BR 127 adhesive bond primer. Wedge tests were also conducted on Al 2024-T3 prepared with PAA/BR 127 and bonded with the evaluated paste adhesives. Polyester random mat scrim cloth (0.004in thick) was used for bondline control with all adhesives except EA 9309.3NA, which is manufactured with glass beads to control bondline thickness to approximately 0.005 inch. All data represent the average of five specimens unless otherwise noted.

2.9.1 Determination of Baseline Adhesive Properties

Evaluation of baseline properties of the various paste adhesives was conducted on phosphoric acid anodized Al 2024-T3 primed with Cytec BR 127 bond primer and tested via tensile lap shear and floating roller peel. BR 127 was applied according to Cytec's recommended procedure to a nominal dry film thickness of 0.0002 inch, dried for 30 minutes at ambient temperature (70°F), and then cured for 60 minutes at 250°F. Adherends were bonded with the epoxy paste adhesives according to manufacturers' recommendations and cured at ambient temperature (70°F $\pm$ 5°F) using either 35 psi positive pressure or 15in Hg vacuum pressure. Vacuum pressure was applied in order to replicate on-aircraft curing conditions. Pressure was applied to the panels for only the first 24 hours. Panels were then held at 70°F for an additional 6 days.

Elevated-temperature curing of paste adhesives is a common repair practice necessitated by the desire to decrease the amount of time required to perform repairs. For this reason, additional lap shear and peel specimens were fabricated using adhesive cured at elevated temperatures recommended by the manufacturers. These temperatures were well below the cure temperatures required for most epoxy film adhesives. Panels bonded at elevated temperature were heated at a rate of 5°F per minute to the recommended cure temperature and held at that temperature for 60 minutes. The recommended cure temperature was 180°F for all adhesives except EA 9394 and EA 9396. The cure temperature for these adhesives was 150°F. Tensile lap shear specimens were tested at 70°F, 160°F, and 180°F. Floating roller peel testing was conducted at 70°F. Failure modes were determined and recorded as percent cohesive failure (within the adhesive layer). Specimens prepared with PAA/BR 127 exhibited varying percentages of interfacial failure between the primer and adhesive but did not fail at the aluminum-primer interface. Results of mechanical testing performed on specimens bonded with adhesives cured at ambient temperature (70°F) under positive pressure are shown in Table 2.9-1. Table 2.9-2 contains the results of mechanical tests for specimens bonded with adhesives cured at elevated temperature under positive pressure. Lap shear and peel test results obtained with adhesives cured at elevated temperature under vacuum pressure are shown in Table 2.9-3.

Table 2.9-1: Comparison of Paste Adhesive Properties when Cured at Ambient Temperature Under Positive Pressure

Adhesive	Lap Shear Strength (psi) (% cohesive failure)			Peel Strength (pli)
	70°F	160°F	180°F	70°F
EA 9309.3NA	4037 (97% co)	754 (94% co)	436 (99% co)	55.9 (100% co)
EA 9320NA	4620 (99% co)	1126 (100% co)	843 (100% co)	23.9 (100% co)
EA 9330.3	4414 (100% co)	764 (100% co)	582 (98% co)	38.4 (100% co)
EA 9394	4076 (94% co)	2522 (100% co)	2697 (100% co)	25.6 (97% co)
EA 9396	5248 (98% co)	3288 (100% co)	2993 (91% co)	24.5 (100% co)
EC-2615	4870 (11% co)	801 (90% co)	714 (39% co)	77.0 (90% co)
EC-3333	3477 (-0-% co)	1087 (-0-% co)	453 (27% co)	75.9 (100% co)

Note: all data are the average of 5 specimens except for EA 9309.3NA (10 specimens)

Table 2.9-2: Comparison of Paste Adhesive Properties when Cured at Elevated Temperature Under 35 psi Positive Pressure

Adhesive	Lap Shear Strength (psi) (% cohesive failure)			Peel Strength (pli)
	70°F	160°F	180°F	70°F
EA 9309.3NA	4872 (40% co)	3142 (90% co)	1274 (60% co)	60.0 (90% co)
EA 9320NA	5756 (99% co)	3597 (81% co)	1708 (84% co)	25.2 (100% co)
EA 9330.3	5344 (93% co)	1022 (86% co)	773 (64% co)	47.6 (100% co)
EA 9394	4857 (78% co)	3126 (84% co)	3141 (84% co)	25.8 (81% co)
EA 9396	4238 (40% co)	4456 (94% co)	3965 (53% co)	17.6 (95% co)
EC-2615	5167 (11% co)	3253 (30% co)	2023 (24% co)	43.6 (3% co)
EC-3333	5177 (2% co)	2919 (32% co)	1690 (14% co)	46.8 (5% co)

Note: all data are the average of 5 specimens except for EA 9309.3NA (10 specimens)

Table 2.9-3: Comparison of Paste Adhesive Properties when Cured at Elevated Temperature Under 15in Hg Vacuum Pressure

Adhesive	Lap Shear Strength (psi) (% cohesive failure)			Peel Strength (pli)
	70°F	160°F	180°F	70°F
EA 9309.3NA	4460 (90% co)	2506 (100% co)	736 (80% co)	52.1 (90% co)
EA 9320NA	5197 (98% co)	3147 (100% co)	1812 (97% co)	27.3 (100% co)
EA 9330.3	5000 (93% co)	729 (88% co)	662 (81% co)	48.1 (100% co)
EA 9394	3818 (93% co)	2926 (95% co)	2798 (98% co)	23.2 (89% co)
EA 9396	3766 (62% co)	3021 (89% co)	2161 (38% co)	13.9 (95% co)
EC-2615	5090 (35% co)	2293 (59% co)	1776 (33% co)	52.5 (5% co)
EC-3333	5225 (13% co)	3280 (36% co)	1810 (13% co)	49.9 (-0-% co)

Note: all data are the average of 5 specimens except for EA 9309.3NA (10 specimens)

Baseline wedge tests were performed on Al 2024-T3 adherends prepared with PAA/BR 127. The adhesives were cured for 60 minutes at 180°F and 35 psi except for EA 9394 and EA 9396, which were cured for 60 minutes at 150°F and 35 psi. Polyester scrim cloth was used for bondline control with all adhesives except EA 9309.3, since it is manufactured with glass beads. Specimens were tested at 120°F and 95-100% relative humidity (RH). Results for the baseline wedge tests are shown in Table 2.9-4.

Table 2.9-4: Baseline Wedge Test Results

Adhesive	Initial (in)	Cummulative Crack Growth (in)							Total (in)	Failure Mode
		1 hr	8 hrs	24 hrs	7 days	14 days	21 days	28 days		
EA 9309.3NA	1.42	0.06	0.10	0.15	0.36	0.43	0.48	0.58	2.00	88% co
	1.33	0.04	0.06	0.10	0.26	0.37	0.50	0.51	1.84	100% co
EA 9320NA	1.59	0.06	0.06	0.07	0.09	0.12	0.15	0.17	1.76	100% co
EA 9330.3	1.38	0.08	0.47	0.73	0.96	1.02	1.06	1.10	2.48	71% co
EA 9394	1.75	0.07	0.16	0.16	0.20	0.22	0.22	0.23	1.98	96% co
EA 9396	1.77	0.07	0.16	0.16	0.29	0.33	0.39	0.42	2.19	100% co
EC-2615	1.33	0.01	0.06	0.14	0.37	0.52	0.60	0.69	2.02	10% co
EC-3333	1.29	0.03	0.18	0.27	0.54	0.67	0.76	0.86	2.15	22% co

Failure modes for specimens fabricated with all of the Hysol adhesives were mostly cohesive (within the adhesive) with small amounts of interfacial failure occurring between the primer and adhesive. However, the 3M Company adhesives exhibited large amounts of interfacial failure between the primer and adhesive. This failure mode was verified by EDX analysis. The 3M adhesives exhibited high peel strengths when compared to the Hysol adhesives but the poor wedge test results and low percentages of cohesive failure are a concern.

The adhesives exhibited a range of mechanical properties. In general, the following trend was observed: as the peel strength of the adhesive increases, the resistance to heat is reduced as exhibited by the reduction in lap shear strength at elevated temperature. It is also seen that curing under vacuum pressure decreases the strength of the bonds. This is likely due to the increased porosity observed in the bondline for vacuum-cured specimens[23]. Finally, a reduction in strength at elevated temperature is detected when curing at ambient temperature compared to elevated-temperature cure. This is likely caused by reduced glass transition temperature (T_g)[24] as a result of the ambient-temperature cure cycle[25]. Overall, the Hysol adhesives exhibited strengths consistent with published data provided by Hysol and exhibited cohesive failure modes whereas the 3M Company adhesives yielded excessive amounts of interfacial failure mode.

2.9.2 Surface Preparation Evaluation

Aircraft aluminum bonded parts, as received from the manufacturer, are typically fabricated utilizing high-performance surface preparations such as acid anodization or elevated-temperature acid etch. Variants of these processes are often specified in Air Force Technical Orders (T.O.s) as the preferred methods for preparing surfaces for adhesive-bonded repair. However, due to the difficulty of performing these surface preparations on aircraft, maintainers across the Air Force desire a convenient ambient-temperature adhesive bonding process capable of delivering acceptable strength and durability. Therefore, the paste adhesives evaluated in this program were tested with three different surface preparations. PAA/BR 127 was used as a standard. A scuff-sand/solvent wipe process was used to replicate a common on-aircraft approach. Finally, an ambient-temperature nylon-pad/sol-gel surface preparation was evaluated. Grit-blasting was not evaluated since it can be problematic in the field environment. Only the PAA specimens were primed.

Bare Al 2024-T3 adherends were used to fabricate all bonded specimens in the surface preparation evaluation. Tensile lap shear, floating roller peel, and wedge tests were conducted to determine initial bond strength and bond moisture durability using the adhesives with each of the

three surface preparations. The scuff-sand/solvent wipe process consisted of degreasing by wiping the adherends with lint-free cloths moistened with acetone, abrading with 100-grit Al_2O_3 abrasive paper using a random orbital sander, and final wiping with acetone to remove residue. The nylon-pad/sol-gel process employed the same acetone degrease step. Adherends were then abraded with 3-inch diameter 3M Company Scotch-Brite™ Roloc™ coarse pads using a 20,000rpm nitrogen-driven rotary grinder. Adherends were not cleaned with solvent after the final abrasion step. Residue was removed using compressed dry, clean, nitrogen. Sol-gel solution was brush-applied keeping the surface wet for 3 minutes and then dried at ambient laboratory conditions for 30 minutes prior to adhesive application.

For all panels, adhesive was mixed according to the manufacturers' recommendations and applied to both bonding surfaces. Polyester random mat scrim cloth was used for bondline control with all adhesives except EA 9309.3NA, since it is manufactured with glass beads for bondline control. All specimens were cured under 15in Hg vacuum pressure in order to replicate on-aircraft curing conditions, unless otherwise noted. Scuff-sand/solvent wipe, nylon-pad/sol-gel, and PAA/BR 127 specimens were heated to elevated temperature to accelerate adhesive cure. A second set of nylon-pad/sol-gel specimens was fabricated with adhesive cured at ambient temperature. These data were compared to controls fabricated using the PAA/BR 127 surface preparation with adhesive cure at ambient temperature under 35 psi positive pressure. The elevated-temperature cure for EA 9394 and EA 9396 was 60 minutes at 150°F. The elevated-temperature cure for the other adhesives was 60 minutes at 180°F. The ambient-temperature cure cycle for all the adhesives was 24 hours at 70°F under pressure followed by an additional 6 days at ambient after removal of pressure. Tensile lap shear specimens were tested at 70°F, 160°F, and 180°F. Floating roller peel testing was conducted at 70°F. Wedge tests were conducted at 120°F and 95-100% RH.

2.9.2.1 Loctite Hysol EA 9309.3NA

Results for tensile lap shear and floating roller peel testing of EA 9309.3NA are shown in Table 2.9-5. For specimens with less than 100% cohesive failure modes, interfacial failure occurred between the primer and adhesive in PAA/BR 127 specimens and between the adhesive and aluminum on the other specimens. When EA 9309.3NA was cured at elevated temperature, the scuff-sand/solvent wipe process exhibited reduced bond strengths and low percentages of cohesive failure. Most noticeably, it can be seen that EA 9309.3NA exhibited high peel strength when bonded to adherends prepared using PAA/BR 127, however, the peel strength is drastically reduced when bonded to the scuff-sand/solvent wipe surface. At all temperatures, the nylon-pad/sol-gel process provided lap shear strengths comparable with those obtained with PAA/BR 127, but exhibited lower percentages of cohesive failure, especially when tested at 160°F and 180°F. However, the peel strengths of the specimens prepared with the nylon-pad/sol-gel process were reduced when compared to PAA/BR 127, and they exhibited a lower percentage of cohesive failure.

Overall, when ambient-temperature cure is compared to elevated-temperature cure, the lap shear strength of the adhesive is drastically reduced as test temperature increases. The nylon-pad/sol-gel process yields lap shear and peel strengths similar to those of PAA/BR 127 tests, but specimens exhibit very low percentages of cohesive failure when tested in lap shear at elevated temperature.

Table 2.9-5: Effect of Surface Preparation on Mechanical Properties of EA 9309.3NA

Surface Preparation		Lap Shear Strength (psi) (% cohesive failure)			Peel Strength (pli)
		70°F	160°F	180°F	70°F
ET	PAA/BR 127	4318* (95% co)	2295* (99% co)	1029* (89% co)	54.4* (88% co)
ET	Scuff-sand/Solvent wipe	4272* (32% co)	1971* (33% co)	751* (0% co)	8.8* (0% co)
ET	Nylon-pad/Sol-gel	4705* (91% co)	2528* (76% co)	1028* (5% co)	43.8* (58% co)
AT	PAA/BR 127 (pp)**	3819 (95% co)	615 (98% co)	439 (99% co)	50.9 (100% co)
AT	Nylon-pad/Sol-gel	3500 (87% co)	580 (3% co)	521 (23% co)	50.9 (100% co)

AT: Ambient-temperature cure — * *Average of 10 specimens*

ET: Elevated-temperature cure — ** *(pp): cured under positive pressure*

Results for the EA 9309.3NA wedge tests are shown in Table 2.9-6. The PAA/BR 127 specimens exhibited cohesive failure modes and the shortest cracks. Any interfacial failure detected on PAA/BR 127 specimens occurred between the adhesive and primer. The nylon-pad/sol-gel specimens exhibited higher percentages of cohesive failure and shorter crack lengths than the scuff-sand/solvent wipe specimens. The interfacial failure modes present in the scuff-sand solvent wipe and nylon-pad/sol-gel specimens occurred between the adhesive and aluminum.

For a given EA 9309.3NA cure cycle, the nylon-pad/sol-gel surface preparation resulted in bonds with similar strengths to those using PAA/BR 127, but with smaller amounts of cohesive failure. The nylon-pad/sol-gel process did not provide the same level of durability as PAA/BR 127 as evidenced by the wedge tests. The nylon-pad/sol-gel surface preparation outperformed scuff-sand/solvent wipe in all tests conducted with EA 9309.3NA.

Table 2.9-6: Effect of Surface Preparation on Wedge Test Results Using EA 9309.3NA

Surface Preparation		Initial (in)	Cummulative Crack Growth (in)							Total (in)	Failure Mode*
			1 hr	8 hrs	24 hrs	7 days	14 days	21 days	28 days		
ET	PAA/BR127	1.45	0.06	0.14	0.19	0.43	0.51	0.58	0.63	2.08	85% co
ET	PAA/BR127	1.39	0.04	0.13	0.20	0.43	0.54	0.61	0.66	2.05	97% co
ET	Scuff-sand/Solvent wipe	1.40	0.68	0.72	0.76	0.93	1.08	1.14	1.15	2.55	0% co
ET	Scuff-sand/Solvent wipe	1.50	1.16	1.17	1.17	1.19	1.21	1.23	1.25	2.75	0% co
ET	Nylon-pad/Sol-gel	1.40	0.07	0.21	0.32	0.65	0.78	0.89	0.99	2.39	28% co
ET	Nylon-pad/Sol-gel	1.46	0.10	0.18	0.21	0.36	0.46	0.53	0.58	2.04	42% co
AT	PAA/BR127 (pp)	1.49	0.12	0.33	0.44	0.62	0.74	0.83	0.88	2.37	100% co
AT	Scuff-sand/Acetone wipe	1.42	0.45	0.47	0.51	0.56	0.64	0.76	0.83	2.25	0% co
AT	Nylon-pad/Sol-gel	1.55	0.13	0.30	0.38	0.86	1.06	1.08	1.10	2.65	74% co

*co: cohesive failure within the adhesive layer

2.9.2.2 Loctite Hysol EA 9320NA

Results of the EA 9320NA tensile lap shear and floating roller peel testing are shown in Table 2.9-7. The small amount of interfacial failure exhibited by some of the PAA/BR 127 specimens occurred between the primer and adhesive. For the other specimens, interfacial failure occurred between the aluminum and adhesive. The scuff-sand/solvent wipe process exhibited significantly reduced lap shear strengths and failure modes. Peel strength for specimens

prepared with the EA 9320NA was almost undetectable when using the scuff-sand/solvent wipe process. Lap shear specimens prepared with the nylon-pad/sol-gel process exhibited very similar bond strengths and failure modes to those of PAA/BR 127-prepared specimens when cured at ambient temperature or elevated temperature and tested at ambient temperature. There was a reduction in the percent cohesive failure for nylon-pad/sol-gel lap shear specimens cured and tested at elevated temperature.

Results for the EA 9320NA wedge tests are shown in Table 2.9-8. The PAA/BR 127 and nylon-pad/sol-gel specimens exhibited excellent failure modes and the shortest cracks. The scuff-sand/solvent wipe specimens resulted in gross adhesional failure at the aluminum-adhesive interface within 24 hours of testing. Overall, the nylon-pad/sol-gel process yielded excellent results in mechanical and durability testing when used with EA 9320NA adhesive, even though the process did not include a primer.

Table 2.9-7: Effect of Surface Preparation on Mechanical Properties of EA 9320NA

Surface Preparation		Lap Shear Strength (psi) (% cohesive failure)			Peel Strength (pli)
		70°F	160°F	180°F	70°F
ET	PAA/BR 127	5197 (98% co)	3147 (100% co)	1812 (97% co)	27.3 (100% co)
	Scuff-sand/Solvent wipe	3366 (60% co)	1954 (23% co)	1040 (-0-% co)	2.7 (-0-% co)
	Nylon-pad/Sol-gel	4807 (99% co)	2970 (80% co)	1667 (50% co)	25.1 (100% co)
AT	PAA/BR 127 (pp)	4620 (99% co)	1126 (100% co)	843 (100% co)	23.9 (100% co)
	Nylon-pad/Sol-gel	3992 (100% co)	1018 (100% co)	734 (100% co)	23.2 (100% co)

Table 2.9-8: Effect of Surface Preparation on Wedge Test Results Using EA 9320NA

Surface Preparation		Initial (in)	Cummulative Crack Growth (in)							Total (in)	Failure Mode*
			1 hr	8 hrs	24 hrs	7 days	14 days	21 days	28 days		
ET	PAA/BR127	1.63	0.05	0.06	0.06	0.06	0.11	0.11	0.11	1.74	100% co
	Scuff-sand/Solvent wipe	1.63	0.49	0.60	0.63	0.69	0.73	0.74	0.75	2.38	-0-% co
	Nylon-pad/Sol-gel	1.64	0.04	0.10	0.10	0.16	0.22	0.26	0.26	1.90	95% co
AT	PAA/BR127 (pp)	1.77	0.16	0.16	0.16	0.18	0.19	0.19	0.2	1.98	100% co
	Nylon-pad/Sol-gel	1.73	0.1	0.1	0.1	0.11	0.12	0.13	0.14	1.88	100% co

* co: cohesive failure within the adhesive layer

2.9.2.3 Loctite Hysol EA 9330.3

Results of the EA 9330.3 tensile lap shear and floating roller peel testing are shown in Table 2.9-9. Although the PAA/BR 127 specimens' failure modes were mostly cohesive, some exhibited partial failures at the primer-adhesive interface. Interfacial failure exhibited by other specimens was between the aluminum and primer. The scuff-sand/solvent wipe process with EA 9330.3 did not result in the significant reductions in ambient-temperature lap shear and peel strengths that were observed using this process with the other adhesives. However, scuff-sand solvent wipe specimens experienced a large reduction in lap shear strength when tested at elevated temperature. These specimens also resulted in complete interfacial failure between the adhesive and metal.

Table 2.9-9: Effect of Surface Preparation on Mechanical Properties of EA 9330.3

Surface Preparation		Lap Shear Strength (psi) (% cohesive failure)			Peel Strength (pli)
		70°F	160°F	180°F	70°F
ET	PAA/BR 127	5000 (93% co)	729 (88% co)	662 (81% co)	48.1 (100% co)
	Scuff-sand/Solvent wipe	4533 (82% co)	441 (-0-% co)	378 (-0-% co)	39.3 (70% co)
	Nylon-pad/Sol-gel	4138 (99% co)	903 (68% co)	666 (48% co)	42.7 (100% co)
AT	PAA/BR 127 (pp)	4414 (100% co)	764 (100% co)	582 (98% co)	38.4 (100% co)
	Nylon-pad/Sol-gel	4262 (100% co)	628 (89% co)	482 (95% co)	36.7 (100% co)

With EA 9330.3 cured at ambient temperature, the nylon-pad/sol-gel specimens yielded similar strengths and failure modes as PAA/BR 127 specimens. However, when the cure of the adhesive was accelerated with heat, specimens prepared with the nylon-pad/sol-gel process exhibited reduced amounts of cohesive failure when tested at elevated temperature, although their strengths were very consistent with that of the PAA/BR 127 specimens. The specimens prepared with the nylon-pad/sol-gel process again outperform those prepared with the scuff-sand/solvent wipe process.

Results for the EA 9330.3 wedge tests are shown in Table 2.9-10. PAA/BR 127 test specimens exhibited excellent failure modes and the shortest cracks. The scuff-sand/solvent wipe specimens resulted in interfacial failure after 28 days of testing. The nylon-pad/sol-gel specimens exhibited a mixed failure mode and longer cracks than the PAA /BR 127 specimens. Overall, the nylon-pad/sol-gel process yielded better results than the scuff-sand/solvent wipe process, but lacked the wedge test durability that PAA/BR 127 provided with EA 9330.3.

Table 2.9-10: Effect of Surface Preparation on Wedge Test Results Using EA 9330.3

Surface Preparation		Initial (in)	Cummulative Crack Growth (in)							Total (in)	Failure Mode*
			1 hr	8 hrs	24 hrs	7 days	14 days	21 days	28 days		
ET	PAA/BR127	1.49	0.22	0.53	0.79	1.21	1.27	1.33	1.37	2.86	87% co
	Scuff-sand/Solvent wipe	1.34	0.29	1.04	1.64	2.45	2.51	2.51	2.56	3.90	-0-% co
	Nylon-pad/Sol-gel	1.41	0.16	0.92	1.32	1.66	1.71	1.75	1.75	3.16	40% co
AT	PAA/BR127 (pp)	1.58	0.55	0.95	1.06	1.25	1.32	1.36	1.41	2.98	100% co
	Nylon-pad/Sol-gel	1.61	0.47	0.93	1.35	1.92	1.98	1.98	1.99	3.60	31% co

* co: cohesive failure within the adhesive layer

2.9.2.4 Loctite Hysol EA 9394

Results of the EA 9394 tensile lap shear and floating roller peel testing are shown in Table 2.9-11. Where failure modes are not cohesive, failure occurred between the primer and adhesive in PAA/BR 127 specimens and between the adhesive and aluminum in the other specimens. EA 9394 specimens exhibited excellent properties when tested at elevated temperature. The EA 9394 also yielded excellent properties when cured at ambient temperature as compared to the other paste adhesives that tended to lose elevated-temperature strength rapidly when cured at ambient. The peel strengths obtained for EA 9394 were slightly high when compared to the manufacturer's published value of 20 pli. These peel strengths are also considerably higher than published results of 10 pli found in previous work conducted at UDRI[26]. As shown with other

paste adhesives, the scuff-sand/solvent wipe surface preparation yielded interfacial failures and lower strengths compared to specimens prepared with PAA/BR 127 and the nylon-pad/sol-gel processes. The poor performance of the scuff-sand/solvent wipe surface preparation was especially evident in the floating roller peel results.

Table 2.9-11: Effect of Surface Preparation on Mechanical Properties of EA 9394

Surface Preparation		Lap Shear Strength (psi) (% cohesive failure)			Peel Strength (pli)
		70°F	160°F	180°F	70°F
ET	PAA/BR 127	3818 (93% co)	2926 (95% co)	2798 (98% co)	23.2 (89% co)
	Scuff-sand/Solvent wipe	2823 (31% co)	2210 (93% co)	2282 (74% co)	3.3 (-0-% co)
	Nylon-pad/Sol-gel	3829 (46% co)	2379 (88% co)	2301 (80% co)	16.7 (79% co)
AT	PAA/BR 127 (pp)	4076 (94% co)	2522 (100% co)	2697 (100% co)	25.6 (97% co)
	Nylon-pad/Sol-gel	3234 (97% co)	2043 (93% co)	2029 (85% co)	25.2 (95% co)

Results for the EA 9394 wedge tests are shown in Table 2.9-12. Initial cracks in the scuff-sand/solvent wipe specimens were at the aluminum-adhesive interface. The average initial crack length for the scuff-sand/solvent wiped specimens were was 2.76 inches as compared to cohesive (within the adhesive) initial cracks exhibited with the PAA/BR 127 and nylon-pad/sol-gel specimens of approximately 1.80 inches. After 28 days in humidity, specimens prepared with the nylon-pad/sol-gel process had smaller crack lengths than the specimens prepared using the scuff-sand/solvent wipe process. The nylon-pad/sol-gel process was not able to achieve the same performance as PAA/BR 127, as shown by the larger crack lengths and lesser amounts of cohesive failure.

Table 2.9-12: Effect of Surface Preparation on Wedge Test Results Using EA 9394

Surface Preparation		Initial (in)	Cummulative Crack Growth (in)							Total (in)	Failure Mode*
			1 hr	8 hrs	24 hrs	7 days	14 days	21 days	28 days		
ET	PAA/BR127	1.89	0.13	0.14	0.16	0.20	0.24	0.24	0.25	2.14	100% co
	Scuff-sand/Solvent wipe	2.76	0.05	0.11	0.11	0.18	0.20	0.21	0.21	2.97	-0-% co
	Nylon-pad/Sol-gel	1.75	0.12	0.23	0.48	0.62	0.69	0.69	0.75	2.50	44& co
AT	PAA/BR127 (pp)	1.88	0.14	0.14	0.15	0.21	0.23	0.23	0.27	2.15	100% co
	Nylon-pad/Sol-gel	1.81	0.22	0.23	0.27	0.48	0.57	0.62	0.70	2.52	38% co

* co: cohesive failure within the adhesive layer

2.9.2.5 Loctite Hysol EA 9396

Results of the EA 9396 tensile lap shear and floating roller peel testing are shown in Table 2.9-13. Again, any interfacial failure exhibited occurred between the primer and adhesive in PAA/BR 127 specimens and between the adhesive and aluminum with the other specimens. In general, higher strengths and better failure modes were obtained when curing EA 9396 at ambient temperature versus the accelerated elevated-temperature cure. This is particularly evident in the peel results. Scuff-sand/solvent wipe specimens resulted in complete adhesional failure between the aluminum and adhesive in all cases. In fact, the peel specimens were not tested because they fell apart during machining. The nylon-pad/sol-gel surface preparation yielded much better results compared to the scuff-sand/solvent wipe process, but did not match the strengths or failure modes achieved by specimens prepared with PAA/BR 127.

Table 2.9-13: Effect of Surface Preparation on Mechanical Properties of EA 9396

Surface Preparation		Lap Shear Strength (psi) (% cohesive failure)			Peel Strength (pli)
		70°F	160°F	180°F	70°F
ET	PAA/BR 127	3766 (62% co)	3021 (89% co)	2166 (38% co)	13.9 (95% co)
	Scuff-sand/Solvent wipe	1287 (-0-% co)	689 (-0-% co)	613 (-0-% co)	Broke during machining
	Nylon-pad/Sol-gel	3550 (28% co)	1736 (30% co)	2148 (24% co)	9.6 (50% co)
AT	PAA/BR 127 (pp)	5248 (98% co)	3288 (100% co)	2993 (91% co)	24.5 (100% co)
	Nylon-pad/Sol-gel	3380 (99% co)	1795 (54% co)	1778 (26% co)	22.0 (85% co)

Results for the EA 9396 wedge tests are shown in Table 2.9-14. The nylon-pad/sol-gel surface preparation yielded larger crack growths than did PAA/BR 127. Specimens fabricated with the nylon-pad/sol-gel process resulted in complete adhesional failure between the aluminum and adhesive when EA 9396 was cured at ambient temperature. Initial cracks in the scuff-sand/solvent wipe specimens were at the aluminum-adhesive interface. The initial cracks were nearly 4.50 inches in length compared to cohesive initial cracks of 1.8 inches. The scuff-sand/solvent wipe specimens failed prior to the one-hour reading. Overall, the scuff-sand/solvent wipe specimens exhibited lower bond strengths, less durability, and complete adhesional failures at all testing conditions. The nylon-pad/sol-gel process provided better strength and durability than the scuff-sand/solvent wipe process, but was unable to meet the performance provided by PAA/BR 127.

Table 2.9-14: Effect of Surface Preparation on Wedge Test Results Using EA 9396

Surface Preparation		Initial (in)	Cummulative Crack Growth (in)							Total (in)	Failure Mode*
			1 hr	8 hrs	24 hrs	7 days	14 days	21 days	28 days		
ET	PAA/BR127	1.89	0.11	0.17	0.17	0.22	0.33	0.35	0.40	2.29	83% co
	Scuff-sand/Solvent wipe	4.46	Fell apart by 1 hour reading							>4.46	-0-% co
	Nylon-pad/Sol-gel	1.97	0.16	0.54	0.66	0.80	0.92	0.92	0.92	2.89	88% co
AT	PAA/BR127 (pp)	1.74	0.13	0.20	0.23	0.34	0.39	0.44	0.45	2.19	100% co
	Nylon-pad/Sol-gel	1.90	0.14	0.73	1.19	1.55	1.58	1.60	1.64	3.54	3% co

* co: cohesive failure within the adhesive layer

2.9.2.6 3M Company EC-2615

Results of the EC-2615 tensile lap shear and floating roller peel testing are shown in Table 2.9-15. Again, any interfacial failure occurred between the primer and adhesive in PAA/BR 127 specimens and between the adhesive and aluminum on the other specimens. EC-2615 yielded better strength at elevated temperature when cured at elevated temperature versus cured at ambient temperature, but exhibited large amounts of interfacial failure, even for PAA/BR 127 specimens. In fact, PAA/BR 127 peel specimens exhibited complete interfacial failure between the primer and adhesive when cured at elevated temperature. The cause for this failure mode was not determined. When cured at ambient temperature, PAA/BR 127 specimens yielded higher percentages of cohesive failure, and much higher peel strengths. The detriment to ambient cure was the reduction in elevated-temperature lap shear strength. Scuff-sand/solvent wipe specimens resulted in complete adhesional failure between the aluminum and adhesive in

all cases. The nylon-pad/sol-gel surface preparation produced much better results than the scuff-sand/solvent wipe process, but did not match the strengths or failure modes achieved with specimens prepared with PAA/BR 127.

Table 2.9-15: Effect of Surface Preparation on Mechanical Properties of EC-2615

Surface Preparation		Lap Shear Strength (psi) (% cohesive failure)			Peel Strength (pli)
		70°F	160°F	180°F	70°F
ET	PAA/BR 127	4255 (62% co)	2195 (56% co)	2179 (30% co)	46.9 (-0-% co)
		5924 (8% co)	2390 (62% co)	1372 (36% co)	58.0 (10% co)
	Scuff-sand/Solvent wipe	3710 (-0-% co)	2283 (-0-% co)	1148 (-0-% co)	1.8 (-0-% co)
	Nylon-pad/Sol-gel	4819 (6% co)	2195 (14% co)	1356 (2% co)	38.0 (-0-% co)
AT	PAA/BR 127 (pp)	4870 (11% co)	801 (90% co)	714 (39% co)	77.0 (90% co)
	Nylon-pad/Sol-gel	4244 (46% co)	1053 (-0-% co)	444 (-0-% co)	60.4 (70% co)

Results for the EC-2615 wedge tests are shown in Table 2.9-16. PAA/BR 127 specimens exhibited interfacial failure between the primer and adhesive. Interfacial failure occurred at the metal-adhesive interface on all other specimens. Overall, more interfacial failure occurred in specimens cured at elevated temperature than those cured at ambient temperature. Scuff-sand/solvent wipe specimens resulted with initial cracks occurring completely at the aluminum-adhesive interface and were removed from humidity after 7 days due to excessive crack length. The initial cracks averaged 2.53 inches in length compared to cohesive initial cracks of approximately 1.5 inches. Overall, the scuff-sand/solvent wipe specimens exhibited lower bond strengths, less durability, and complete adhesional failures at all testing conditions. The nylon-pad/sol-gel process provided better strength and durability than the scuff-sand/solvent wipe process, but was unable to meet the performance provided by PAA/BR 127.

Table 2.9-16: Effect of Surface Preparation on Wedge Test Results Using EC-2615

Surface Preparation		Initial (in)	Cummulative Crack Growth (in)							Total (in)	Failure Mode*
			1 hr	8 hrs	24 hrs	7 days	14 days	21 days	28 days		
ET	PAA/BR 127	1.52	0.00	0.03	0.04	0.16	0.25	0.31	0.38	1.90	64% co
	Scuff-sand/Solvent wipe	2.53	1.46	1.47	1.47	1.47	removed due gross failure			4.00	-0-% co
	Nylon pad / sol-gel	1.60	0.01	0.06	0.15	0.55	0.76	0.93	1.07	2.67	5% co
AT	PAA/BR127 (pp)	0.97	0.09	0.31	0.38	0.56	0.61	0.66	0.7	1.66	99% co
	Nylon-pad/Sol-gel	0.93	0.14	0.28	0.36	0.64	0.74	0.82	0.86	1.79	43% co

* co: cohesive failure within the adhesive layer

2.9.2.7 3M Company EC-3333

Results of the EC-3333 tensile lap shear and floating roller peel testing are shown in Table 2.9-17. All interfacial failure occurred between the primer and adhesive for PAA/BR 127 specimens and between the adhesive and aluminum on the other specimens. As was the case for EC-2615, EC-3333 yielded better lap shear strength at elevated temperature when cured at elevated temperature, but exhibited large amounts of interfacial failure, even in PAA/BR 127 specimens. PAA/BR 127 peel specimens exhibited complete interfacial failure between the primer and adhesive when cured at elevated temperature. Curing at ambient temperature did not seem to improve the amount of cohesive failure detected in lap shear specimens but drastically improved the strength and failure modes in peel tests. PAA/BR 127 specimens yielded the best

lap shear and peel strengths when cured at elevated temperature. Scuff-sand/solvent wipe specimens resulted in reduced bond strengths, especially in peel, and complete adhesional failure between the aluminum and adhesive in all cases. The nylon-pad/sol-gel surface preparation produced much better results than the scuff-sand/solvent wipe process, but did not match the strengths or failure modes achieved with specimens prepared with PAA/BR 127.

Table 2.9-17: Effect of Surface Preparation on Mechanical Properties of EC-3333

Surface Preparation		Lap Shear Strength (psi) (% cohesive failure)			Peel Strength (pli)
		70°F	160°F	180°F	70°F
ET	PAA/BR 127	4960 (20% co)	3500 (52% co)	2180 (6% co)	44.3 (-0-% co)
		5489 (6% co)	3059 (20% co)	1439 (20% co)	55.4 (-0-% co)
	Scuff-sand/Solvent wipe	4134 (-0-% co)	1825 (-0-% co)	600 (-0-% co)	2.6 (-0-% co)
	Nylon-pad/Sol-gel	4894 (12% co)	2525 (23% co)	964 (-0-% co)	38.3 (-0-% co)
AT	PAA/BR 127 (pp)	3477 (-0-% co)	1087 (-0-% co)	453 (27% co)	75.9 (100% co)
	Nylon-pad/Sol-gel	5281 (57% co)	877 (-0-% co)	729 (-0-% co)	57.8 (80% co)

Results for the EC-2615 wedge tests are shown in Table 2.9-18. PAA/BR 127 specimens exhibited interfacial failure between the primer and adhesive. Interfacial failure occurred at the metal-adhesive interface on all other specimens. All specimens demonstrated adhesional failures except for those with PAA/BR 127. Specimens prepared with the scuff-sand/solvent wipe procedure exhibited initial cracks at the aluminum-adhesive interface. These cracks averaged 2.55 inches in length compared to cohesive initial cracks of about 1.4 inches. Overall, the scuff-sand/solvent wipe specimens produced lower bond strengths, less durability, and complete adhesional failures at all testing conditions. The nylon-pad/sol-gel process provided better strength and durability than the scuff-sand/solvent wipe process, but was unable to meet the performance provided by PAA/BR 127.

Table 2.9-18: Effect of Surface Preparation on Wedge Test Results Using EC-3333

Surface Preparation		Initial (in)	Cummulative Crack Growth (in)							Total (in)	Failure Mode*
			1 hr	8 hrs	24 hrs	7 days	14 days	21 days	28 days		
ET	PAA/BR127	1.4	0.01	0.04	0.08	0.25	0.38	0.46	0.51	1.91	47% co
	Scuff-sand/Solvent wipe	2.55	0.68	0.68	0.68	0.72	0.74	0.84	0.86	3.41	-0-% co
	Nylon-pad/Sol-gel	1.21	0.06	0.16	0.24	0.45	0.57	0.67	0.74	1.95	-0-% co
AT	PAA/BR127 (pp)	1.07	0.08	0.36	0.47	0.64	0.66	0.72	0.76	1.83	76% co
	Nylon-pad/Sol-gel	1.01	0.16	0.33	0.41	0.64	0.78	0.84	0.91	1.92	-0-% co

* co: cohesive failure within the adhesive layer

2.9.3 Repeatability Assessment

In order to determine the repeatability of the nylon-pad/sol-gel surface preparation using EA 9320NA, an assessment was conducted using tensile lap shear and wedge tests. Five wedge test panels (tested at 120°F & 95-100% RH) and ten lap shear panels (five tested at 70°F and five tested at 160°F) were fabricated with each of the following surface preparations: grit-blast/sol-gel[27], nylon-pad/sol-gel, and PAA/BR 127 (control). Neither sol-gel surface preparation included an adhesive bond primer. Al 7075-T6 adherends were used in this assessment as opposed to Al 2024-T3. Adherends were degreased by wiping with lint-free cloths moistened with acetone. Nylon-pad abraded panels were deoxidized with 3-inch diameter 3M Company

Scotch-Brite™ Roloc™ medium pads using a 20,000rpm nitrogen-driven rotary grinder. Grit-blasted panels were blasted with 50-micron Al_2O_3 grit. All panels were blown with 35 psi nitrogen to remove residual grit or residue prior to application of sol-gel solution. Sol-gel solution was brush applied so the surface was kept wet for 3 minutes. Panels were allowed to dry at ambient laboratory conditions (70°F and 60% RH) for 30 minutes prior to application of adhesive. Adhesive was applied on both bonding surfaces and a random-mat polyester scrim cloth was used for bondline control. Panels were cured for 2 hours at 150°F and 15in Hg vacuum pressure. Results of the ambient-temperature tensile lap shear testing are shown in Figure 2.9-1. It can be seen from the figure there was little change in lap shear strength or failure mode associated with surface preparation. The results are particularly encouraging since they were repeated with five separate panels (25 specimens) under more difficult conditions: 7075-T6 aluminum as opposed to 2024-T3 and medium abrasive pads rather than coarse.

Results of the lap shear testing conducted at 160°F are shown in Figure 2.9-2. The lap shear strength of the bond drops with increasing temperature. However, the average strengths of the bonds prepared with the different surface preparations are relatively the same. There is a drop of percent cohesive failure mode when using both the grit-blast and nylon-pad sol-gel processes when compared to PAA/BR 127. The small amount of adhesional failure occurred between the aluminum and adhesive. Results appear to be reproducible within the five panels.

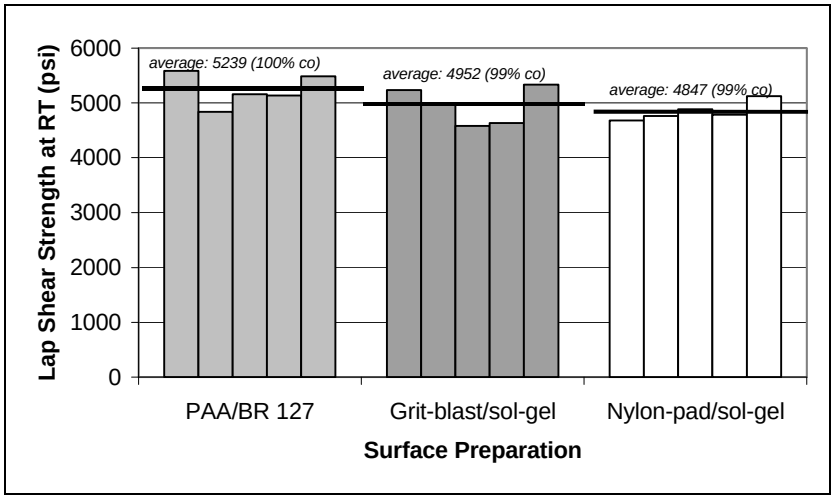


Figure 2.9-1: Effect of Surface Preparation on Ambient-Temperature Lap Shear Strength Using EA 9320NA

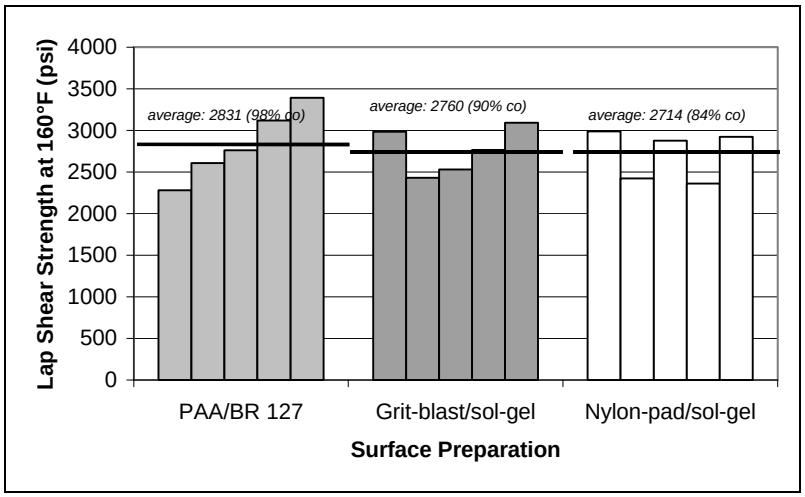


Figure 2.9-2: Effect of Surface Preparation on Lap Shear Strength at 160°F Using EA 9320NA

Results for the wedge tests are shown in Table 2.9-19. The nylon-pad/sol-gel process did not result in the same failure modes as the grit-blast/sol-gel and PAA/BR 127 processes. However, there did appear to be repeatability within each of the processes. Since the data using the nylon-pad/sol-gel process without primer led to less than the desired (100% cohesive failure), the tests were repeated varying the coarseness of the Scotch-Brite™ Roloc™ pads. Two panels were fabricated per testing condition with both coarse and medium grade Roloc™ pads. Results of the ambient-temperature lap shear testing are shown in Figure 2.9-3. Results for lap shear tests conducted at 160°F are shown in Figure 2.9-4.

Table 2.9-19: Effect of Surface Preparation on Wedge Test Results Using EA 9320NA

Surface Preparation	Initial (in)	Cummulative Crack Growth (in)							Total (in)	Failure Mode*
		1 hour	8 hour	24 hour	7 day	14 day	21 day	28 day		
PAA / BR 127	1.64	0.06	0.10	0.11	0.12	0.13	0.14	0.16	1.80	100% co
	1.67	0.05	0.07	0.09	0.09	0.09	0.09	0.10	1.77	100% co
	1.65	0.07	0.08	0.09	0.11	0.13	0.14	0.14	1.79	100% co
	1.66	0.06	0.07	0.08	0.12	0.14	0.14	0.17	1.83	100% co
	1.77	0.04	0.08	0.09	0.09	0.11	0.11	0.12	1.89	100% co
Grit-blast / Sol-Gel	1.70	0.06	0.12	0.15	0.20	0.22	0.22	0.22	1.92	100% co
	1.75	0.09	0.12	0.14	0.16	0.18	0.18	0.18	1.93	99% co
	1.76	0.09	0.12	0.12	0.14	0.19	0.20	0.20	1.96	100% co
	1.73	0.05	0.09	0.11	0.15	0.21	0.23	0.25	1.98	100% co
	1.71	0.07	0.10	0.11	0.14	0.16	0.22	0.22	1.93	100% co
Nylon Pad / Sol-Gel	1.73	0.05	0.12	0.17	0.21	0.22	0.25	0.25	1.98	82% co
	1.65	0.05	0.17	0.18	0.21	0.23	0.27	0.28	1.93	80% co
	1.69	0.04	0.11	0.11	0.16	0.19	0.22	0.24	1.93	76% co
	1.76	0.05	0.10	0.14	0.18	0.22	0.25	0.26	2.02	87% co
	1.68	0.08	0.11	0.12	0.16	0.25	0.25	0.25	1.93	99% co

* co: cohesive failure within the adhesive layer

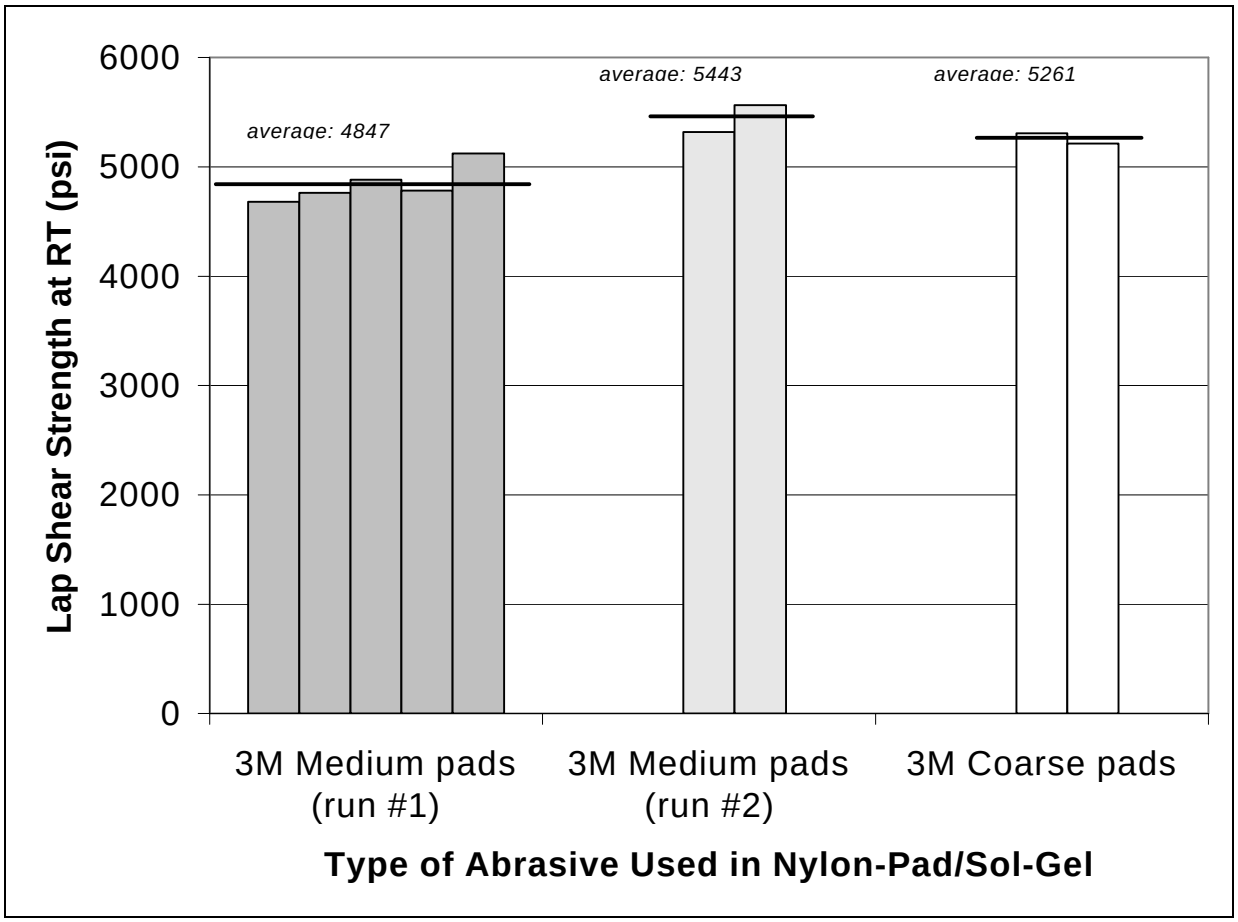


Figure 2.9-3: Effect of Nylon Pad Coarseness on Ambient-Temperature Lap Shear Strength Using EA 9320NA

The ambient-temperature lap shear data from Figure 2.9-3 do not seem to distinguish a difference between the different abrasive pads. Failure modes were all cohesive. However, changes in failure modes were detected when tested at 160°F (see Figure 2.9-4). Use of medium Roloc™ pads resulted in 84% cohesive failure in the first run (data from Figure 2.9-2), and these data was verified in the second run with an average of 86% cohesive failure. When using coarse pads, the failure mode increased to 99% cohesive. There was little difference in strength noticed between specimens prepared with different grades of nylon pads even though there were changes in the amount of cohesive failure present.

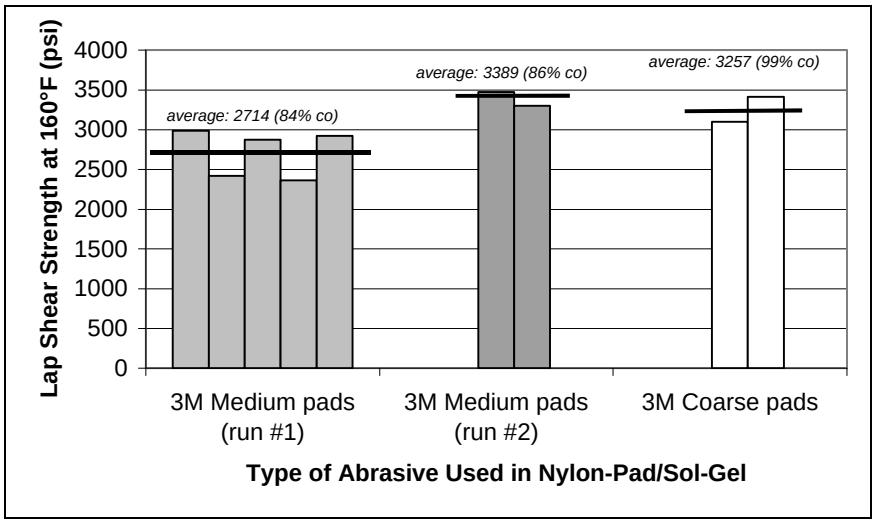


Figure 2.9-4: Effect of Nylon Pad Coarseness on Lap Shear Strength at 160°F Using EA 9320NA

Results for the wedge tests are shown in Table 2.9-20. The failure modes appear to be consistent when using medium pads when comparing Run #1 to Run #2. In both cases, failure modes were about 85-89% cohesive. However, the crack growth was smaller in Run #2 when using medium pads compared to Run #1. When using coarse pads, the amount of cohesive failure increased a small amount to an average value of 93% cohesive.

Table 2.9-20: Effect of Nylon Pad Coarseness on Wedge Test Results Using EA 9320NA

Roloc Pad	Initial (in)	Cummulative Crack Growth (in)							Total (in)	Failure Mode*
		1 hour	8 hour	24 hour	7 day	14 day	21 day	28 day		
Meduim Run #1	1.64	0.06	0.10	0.11	0.12	0.13	0.14	0.16	1.80	100% co
	1.67	0.05	0.07	0.09	0.09	0.09	0.09	0.10	1.77	100% co
	1.65	0.07	0.08	0.09	0.11	0.13	0.14	0.14	1.79	100% co
	1.66	0.06	0.07	0.08	0.12	0.14	0.14	0.17	1.83	100% co
	1.77	0.04	0.08	0.09	0.09	0.11	0.11	0.12	1.89	100% co
Meduim Run #2	1.67	0.05	0.07	0.07	0.08	0.10	0.10	0.12	1.79	90% co
	1.65	0.05	0.05	0.07	0.11	0.11	0.13	0.13	1.78	88% co
Coarse	1.66	0.05	0.07	0.12	0.16	0.16	0.17	0.17	1.83	93% co
	1.73	0.05	0.08	0.09	0.12	0.12	0.14	0.16	1.89	92% co

* co: cohesive failure within the adhesive layer

2.9.4 Evaluation of the Ambient-Temperature Nylon-pad/Sol-Gel Process

In order to estimate the overall effect of surface preparation for each adhesive, a chart comparing the average percent cohesive failure for all lap shear, peel, and wedge test specimens for each process investigated in the surface preparation evaluation is shown in Figure 2.9-5. This was a qualitative comparison based solely on failure modes. Since it includes lap shear, peel, and wedge data, it is possible that one test, such as the wedge test, can have a large influence on the results. The PAA/BR 127 process yields the highest average amount of cohesive failure for each adhesive. This process was also the only one that included an adhesive bond primer. The nylon-pad/sol-gel process yields a higher average amount of cohesive failure than the scuff-

sand/solvent wipe process for every adhesive. For all adhesives tested, the nylon-pad/sol-gel process provided a reduced amount of cohesive failure when compared to PAA/BR 127. The reason for the better performance obtained with EA 9320NA was not determined. However, when using EA 9320NA, the nylon-pad/sol-gel process yielded an average of roughly 92% cohesive failure mode, when compared to the 97% cohesive mode routinely achieved with PAA/BR 127. This was the best failure mode achieved using the nylon-pad/sol-gel process with any of the paste adhesives. Specimens prepared with the nylon-pad/sol-gel surface preparation performed very similarly to those prepared with PAA/BR 127 when bonded with EA 9320NA, as detailed in section 2.9.2.2. The 3M adhesives exhibited extremely low percentages of cohesive failure for all surface preparations when compared to the Hysol adhesives.

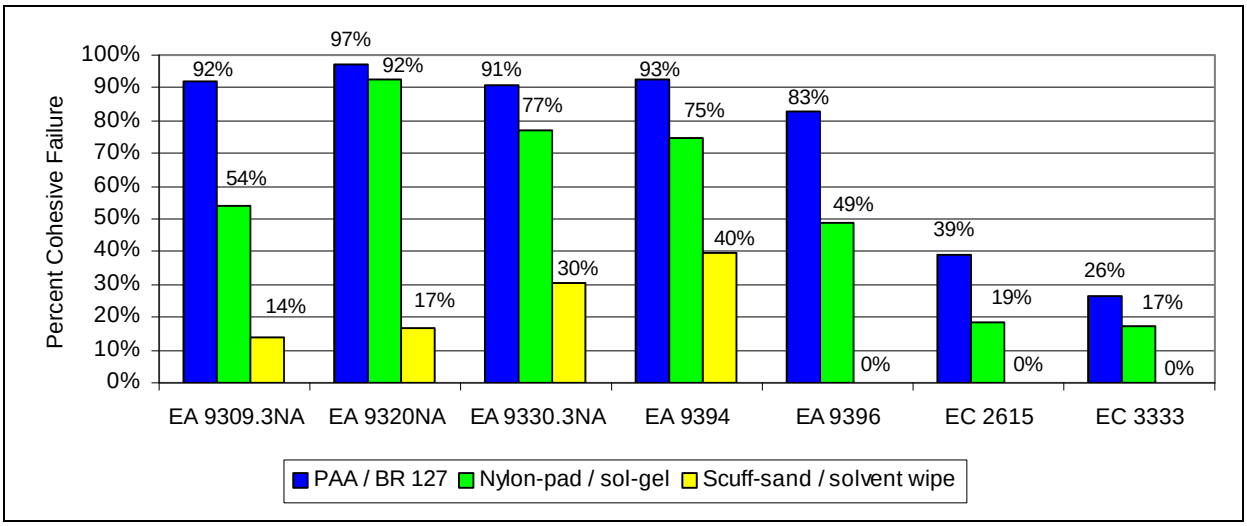


Figure 2.9-5: Average Percent Cohesive Failure versus Surface Preparation for Various Paste Adhesives

3 ADHESIVE BONDING - TITANIUM SUBSTRATES

The bonding of titanium using standard surface preparation techniques has not always been an easy or reproducible process for aerospace hardware. The very passive nature of titanium and the difficulty involved in chemical processing of titanium alloys have forced manufacturers to minimize the use of bonded titanium parts for primary or secondary structure. Several programs have used titanium bonding successfully; however, the surface preparation techniques employed are often arduous and involve hazardous chemicals and processes. Using Boegel-EPII processes, durable bonded interfaces on titanium alloys can be achieved for both original equipment manufacturer (OEM) applications and rework and repair. Methods for promoting adhesion of titanium hardware to epoxy adhesives and coatings were developed and are successfully being implemented at Boeing in several areas.

3.1 Testing and Materials

A number of materials and processes were evaluated during this effort. In most cases, the details for the processing associated with the evaluations are given for each test. At times, full details for parameters held constant are not provided. Unless otherwise noted, test results are the average of 5 specimens taken from one bonded Ti-6Al-4V panel. Grit-blasting was typically performed using 80 micron (#180) alumina. Abrasive papers are often referred to as "sandpapers" even though grit was SiC, ZrO_2, or Al_2O_3. The basic Boegel-EPII formulation or a modified version with added surfactant was used for all tests. Treated surfaces were kept wet with the sol-gel solution for approximately 2 minutes. Cytec BR 6747-1 waterborne, chromated bond primer (20% solids) was used, unless otherwise indicated. For baseline specimens, the primer was applied via an HVLP spray gun to a nominal thickness of 0.1-0.3 mil (0.0001-0.0003 inch), dried for 30 minutes at ambient temperature, and cured for 60 minutes at 250°F in an air-circulating oven. Baseline specimens were bonded with 3M Company AF 163-2M (0.06psf) modified epoxy film adhesive that was autoclave cured for 60 minutes at 250°F under 35-45 psi. In most cases, the one-side tacky (OST) version was used, but this is not separately noted. The wedge test was conducted at 140°F, unless stated otherwise.

3.2 Grit-Blast Surface Activation

3.2.1 Grit-Blasting Parameters

A series of #180 alumina grit-blasted titanium wedge test specimens were prepared to evaluate: 1) the effects of using cleaned and blasted Ti-6Al-4V panels rather than HF/HNO_3 deoxidized panels; 2) the effect of blasting from a distance of either 4 inches or 6 inches; and 3) the effect of air drying (ambient curing) or heat curing of the applied Boegel-EPII coating. The details of the test matrix are shown in Table 3.2-1. All grit-blasting was performed at an angle of 45°. Surface roughness of blasted titanium varied considerably but averaged about 35μin R_a. A Boegel-EPII solution was brush-applied to each of the substrates for two minutes. All samples were coated with BR 6747-1 using an HVLP spray gun. Wedge tests were conducted at 140°F and 98% RH, and results are shown in Table 3.2-2.

Table 3.2-1: #180 Alumina Grit-blasted Ti 6Al-4V Sample Preparation Details

Sample Number	Substrate Condition	Grit-blasting Distance	Boegel EP II Cure Method	Air Drying Time Before Priming
S 61-1A	Deoxidized	6 inches	Air Dried	94 Minutes
S 61-1B	Deoxidized	6 inches	30 Minutes at 250°F	59 Minutes
S 61-2A	Deoxidized	6 inches	Air Dried	82 Minutes
S 61-2B	Cleaned & Degreased	6 inches	Air Dried	76 Minutes
S 61-3A	Deoxidized	4 inches	Air Dried	70 Minutes
S 61-3B	Cleaned & Degreased	4 inches	Air Dried	64 Minutes

Table 3.2-2: Effect of Grit-Blasting Parameters on Ti 6Al-4V Wedge Test Results

Sol-gel Processing Condition	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr	
S 61-1A: Deoxidized Substrates, 6in Grit-Blast (GB) Distance, Air Dried	0.69	0.05	0.10	0.11	0.11	0.12	0.12	97% co
S 61-1B: Deoxidized Substrates, 6in GB Distance, 30min Sol-gel Bake @ 250°F	0.69	0.04	0.12	0.12	0.14	0.15	0.15	78% co
S 61-2A: Deoxidized Substrates, 6in GB Distance, Air Dried	0.76	0.06	0.11	0.11	0.12	0.12	0.12	93% co
S 61-2B: Cleaned & Degreased Substrates, 6in GB Distance, Air Dried	0.74	0.08	0.14	0.14	0.14	0.16	0.16	97% co
S 61-3A: Deoxidized Substrates, 4in GB Distance, Air Dried	0.67	0.11	0.15	0.17	0.19	0.19	0.19	98% co
S 61-3B: Cleaned and Degreased Substrates, 4in GB Distance, Air Dried	0.72	0.00	0.11	0.13	0.16	0.16	0.16	93% co

* co: cohesive failure within the adhesive layer

Grit-blasting at distances of either 4 inches or 6 inches did not appear to have an effect on the failure mode of HF/HNO_3 deoxidized samples. Panels that were alkaline cleaned, but not acid deoxidized, had slightly better failure modes when grit-blasted from a 6-inch rather than a 4-inch distance. The method of drying the sol-gel coatings resulted in differences in the test specimen failure modes of the test specimens. The sample with the worst failure mode, S 61-1B with 78% cohesive failure, was heated at 250°F for 30 minutes to cure the sol-gel coating. All the S 61 series samples that were air-dried prior to priming exhibited cohesive failure mode values between 93% and 98%.

3.2.2 Wet Grit-Blast Study

Grit-blasting with water added to the blast media was evaluated as an alternate grit-blast technique. By adding water to the slurry, it is possible that less grit will be imbedded in the metal surface. Surface profilometry was performed on the two wet grit-blasted panels produced by the Navy. The surface roughness was 31-32μin R_a. The panels were coated with sol-gel and primed with Cytec BR 6747-1. The wedge test results for the wet grit-blasted Ti-6Al-4V panels are given in Table 3.2-3. The specimens were wet grit-blasted weeks before they were sol-gelled and primed, which may account for the poor failure mode.

Table 3.2-3: Effect of Wet Grit-Blasting on Ti-6Al-4V Wedge Test Results

Processing Prior to Sol-Gel	Initial (in)	Cumulative Crack Length (in)						Failure Mode*
		24	168	336	504	672	1008	
Wet Grit Blasting, #180 grit alumina	0.74	0.84	0.87	0.88	0.90	0.91	0.92	60% co
Dry Grit Blasting, #180 grit alumina	0.68	0.78	0.78	0.79	0.80	0.81	0.81	100% co

* co: cohesive failure within the adhesive layer

3.3 Manual Deoxidation Screening Testing

For some repair situations on titanium, grit-blasting is not possible. For these scenarios, a Scotch-Brite™ abrasion or a sandpaper abrasion process can be used to manually deoxidize the surface. In this study, several sets of Ti-6Al-4V specimens were processed using grit-blast, sanding, and flapwheel pretreatments followed by application of the Boegel-EP solution to compare how well each method activated the surface for bonding with the sol-gel coating. Sample preparation is described in Table 3.3-1. Navy contract personnel prepared half of the panels and Boeing personnel prepared half. All of the panels were primed with Cytec BR 6747-1. The specimens prepared by the Navy personnel were brought back to NAVAIR at Patuxent River MD, to be bonded and tested in their laboratories. Likewise, the Boeing-processed panels were bonded and tested at Boeing facilities. Lap shear results are also listed in Table 3.3-1. Wedge test results are depicted in Table 3.3-2.

Table 3.3-1: Titanium Manual Deoxidation Screening Study Lap Shear Results

Sample #	Surface Prep	Sol-Gel	Primer	RT Lap Shear (psi)
R17-1	#180 alumina grit-blasted	Boegel-EPII	Cytec BR 6747-1	6448
R17-2	HF/HNO_3 etched	Boegel-EP	Cytec BR 6747-1	6772
R17-3	HF/HNO_3 etched followed by a #240 grit flap wheel abrade	Boegel-EP	Cytec BR 6747-1	6902
R17-4	HF/HNO_3 etched followed by a #220 alumina sandpaper	Boegel-EP	Cytec BR 6747-1	6720

Table 3.3-2: Ti-6Al-4V Manual Deoxidation Screening Study Wedge Test Results Titanium

Processing Prior to Sol-Gel	Initial (in)	Cumulative Crack Growth (in)					
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr
R 17-1: #180 Alumina Grit Blasted	0.68	0.10	0.10	0.11	0.11	0.13	0.13
R 17-2: HF/HNO3 Etched	1.44	0.22	0.24	0.28	0.28	0.29	0.29
R 17-3: #240 Alumina Flap Wheel Abraded	0.80	0.10	0.32	0.47	0.53	0.56	0.56
R 17-4: #220 Alumina Sandpaper Abraded	0.77	0.08	0.18	0.21	0.33	0.36	0.37

The initial crack length was within the acceptable range for all of the specimens with the exception of the HF/HNO_3-etched specimens. In that case, the initial crack was over twice as long as is typical, and the crack length increased in hot/wet exposure. Boeing has not always been able to achieve reproducible results on acid etched panels, but have not yet attributed the performance to any one particular parameter.

3.4 "Sanding" Variations

A series of test specimens was prepared by abrading HF/HNO_3-etched panels with two pieces of #400 SiC paper per panel. Each piece of "sandpaper" was used for 30 seconds and then discarded. An electric orbital sander was used during the sanding process. The performance of these and other related samples is shown in Table 3.4-1.

These first attempts to roughen Ti 6Al-4V panels with sanding methods deliberately made use of the same abrading procedures used to prepare Al 2024-T3 specimens. These results may indicate that either coarser grit sandpapers, longer periods of sanding, or increased/decreased pressure during the sanding process are required for abrasion of titanium substrates.

Table 3.4-1: Effect of Sanding Methods on Ti- 6Al-4V Wedge Test Results

Processing Prior to Sol-Gel	Initial (in)	Cumulative Crack Growth (in)					
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr
R 17-4 #220 Al_2O_3 Sanded	0.77	0.18	0.21	0.33	0.36	0.38	0.39
R-45-6 Sanded With #400 SiC Paper and Boegel-EP Coated	0.85	0.23	0.48	0.52	0.56	0.56	0.56

3.5 Scotch-Brite™ Roloc™ Disc Abrasion Testing

3.5.1 Initial Scotch-Brite™ Testing

Several types of Scotch-Brite™ pads were investigated: very fine, medium, and coarse. The wedge test results for the various abrasion methods are shown in Table 3.5-1. Abrasion with the coarse or medium pads appears to yield the smallest crack extensions in the wedge test at 0.18 inch and 0.11 inch, respectively. However, the medium pads produced 90% cohesive failure while the failure mode varied from 0% to 75% cohesive when the coarse pads were used.

Table 3.5-1: Effect of Scotch-Brite™ Abrasion Materials on Ti-6Al-4V Wedge Test Results

Processing Prior to Sol-Gel	Initial (in)	Cumulative Crack Growth (in)			Failure Mode
		24hr	168hr	672hr	
Coarse Scotch-Brite™ Roloc™ Abraded	0.78	0.04	0.12	0.95	55% co
Medium Scotch-Brite™ Roloc™ Abraded	0.77	0.03	0.05	0.11	90% co
Very Fine Scotch-Brite™ Roloc™ Abraded	0.80	0.03	0.15	0.20	30% co

*co: cohesive failure within the adhesive layer

3.5.2 Validation of Manual Abrasion Methods

An additional evaluation was conducted at another site to compare three methods of titanium substrate deoxidation and alternatives to grit blasting. The samples identified in the table below as "alumina" were abraded using the 3M Stikit Gold Disc P-180 grade alumina abrasive paper using an air grinder at approximately 4000rpm to remove surface oxidation. Panels were abraded in one direction, turned 90° and abraded again, turned 90° and abraded again, then turned 90° and abraded one final time. Each surface saw four passes of the abrasive to assure good surface preparation, and the sanding disc was changed at each turn. The samples identified in the table as "Roloc™" were abraded using a five inch 3M Scotch-Brite™ Roloc™ Surface Conditioning Disc, Maroon Grade A Medium, using an air drill at approximately 2000rpm. As with the panels above, they were sanded four times, each after turning 90° from the previous time. Finally, a set was prepared using five-inch Merit Abrasive Products Shur-Stik 120 grit zirconia following the same pattern as the other panels and identified in the table as "zirconia."

After abrasion, the panels were blown with oil-free, dry air prior to application of the sol-gel solution. Boegel-EPII was applied with an HVLP spray gun with enough spraying to keep the panel surface wet for three minutes. Panels were sprayed and dried in a nearly vertical position. The sol-gel was dried for about thirty minutes at ambient condition with occasional tipping of the panels to fully vertical to aid in runoff. In addition to the panels prepared with BR 6747-1 primer, some specimens were prepared without primer. For those with primer, the BR 6747-1 was also applied with the HVLP spray gun to a thickness of 0.1-0.3 mil and dried at ambient conditions for about 30 minutes. These were then cured at 250°F for 60 minutes and cooled to ambient prior to lay-up with adhesive. Those samples prepared without primer were laid up with adhesive within 30 minutes of the sol-gel drying. All panels were bonded with AF 163-2K film adhesive and cured at 250°F under 40 psi for 60 minutes. Wedge test specimens were conditioned at 140°F and 95-100% RH. Results are shown in Table 3.5-2.

Table 3.5-2: Wedge Test Results for Titanium with Various Abrasion Techniques

Titanium	Initial	Cumulative Crack Growth (in)									
	(in)	1 hr	4 hr	8 hr	24 hr	48 hr	7 days	14 days	21 days	28 days	56 days
Roloc™ No Primer	0.76	0.00	0.24	0.33	0.46	0.54	0.70	0.99	1.06	1.13	1.34
Roloc™ with Primer	0.73	0.00	0.11	0.17	0.25	0.29	0.36	0.46	0.49	0.50	0.56
Alumina No Primer	0.73	0.01	0.19	0.26	0.43	0.51	0.85	1.03	1.15	1.25	1.43
Alumina with Primer	0.76	0.00	0.06	0.07	0.10	0.13	0.18	0.22	0.27	0.29	0.32
Zirconia with Primer	0.75	0.00	0.06	0.07	0.09	0.10	0.12	-	0.16	0.20	0.27

As would be expected, specimens with primer performed better than specimens without bond primer for both of the surface treatments. In addition, comparing either sanding treatment to Roloc™ showed a clear preference for sanding with the zirconia samples showing slightly better crack growth results than the alumina. However, the failure modes for these samples are not as promising. While the primerless samples showed 0% cohesive failure, even the "best" zirconia samples showed no better than 75-80% cohesive failure. More optimization work needs to be carried out to define reproducible manual abrasion techniques on titanium alloys.

3.6 Bonding Development for Original Equipment Manufacturer (OEM) Applications

For production use, the surface pretreatment chosen has to be suitable for continuous manufacture of multiple parts in a low-cost fashion. Thus, the use of touch labor in processes such as grit-blast, unless done robotically, would be largely unsuitable. For an initial process, Boeing chose to use an alkaline pretreatment based on the Turco® 5578 (Henkel Surface Technologies Corporation) sodium hydroxide chemistries to provide a suitable surface chemistry and morphology for producing durable bonds to the sol-gel chemistry.

3.6.1 Comparison of Chemical Pretreatments to Mechanical Pretreatments

Initial wedge test results for Ti-6Al-4V samples using original equipment manufacturer (OEM) CAA (BAC5890) surface preparation processing prior to sol-gel coating were obtained and compared against other Ti 6Al-4V samples using various deoxidation methods with sol-gel treatment. These performance comparisons are shown in Table 3.6-1.

Table 3.6-1: Comparison Between Chemical Pretreatments and Sol-Gel Surface Preparations for Ti-6Al-4V

Processing Prior to Sol-Gel	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr	
R 17-1 # 180 alumina grit blasted	0.68	0.10	0.10	0.11	0.12	0.13	0.13	100% co
R 73-7 Abraded 3 Min. / Panel With One Brown CRS Scotch-Brite™ Roloc™ Disc	0.74	0.07	0.17	0.17	0.17	0.17	0.19	90% co
R87-3 HF/HNO3 / Turco® 5578 pretreatment	0.72	0.07	0.09	0.09	0.09	0.10	0.10	100% co
Chromic Acid Anodize (with BR 127/FM 73	0.80	0.04	0.05	0.09	0.09	0.09	0.09	100% co

co: cohesive failure within the adhesive layer

The performance of the grit-blast and Turco® 5578 samples and that of the sample given the OEM surface preparation appear to be nearly identical. The Turco® 5578 alkaline etching process leaves the substrates with a surface finish that is only slightly duller than it was just after the HF/HNO_3 etch step. The grit-blasted panels, in comparison, are visibly rough and completely nonspecular in appearance.

3.6.2 Turco® 5578 Pretreatment Evaluations

A series of Ti 6-4 samples were prepared to determine how variations in the titanium OEM process affected wedge crack test performance. The treatments evaluated were three different concentrations of the Turco® 5578 alkaline etching solution with and without the addition of a hot nitric acid desmut after etching. Air-drying versus heat-curing (250°F for 30 minutes) after spray application of the Boegel-EPII solution was also evaluated. Table 3.6-2 lists the various treatments used in the preparation of these samples.

The wedge test results for Turco® 5578-etched Ti-6Al-4V samples after 1000 hours of humidity exposure are shown in Table 3.6-2. The samples that were conditioned in the highest concentration Turco® 5578 solutions performed slightly better than those etched in lower concentration solutions. The HNO_3 desmut treatment on these slow-growth samples appears to have had little effect.

Table 3.6-2: Ti 6-4 Turco® Pretreatment Process Sample Treatments

Sample Number	Turco® 5578 Concentration	HNO_3 Desmut	Boegel-EP II Drying Method
R 137-1A	20 %	Yes	30 Minutes at 250°F
R 137-1B	20 %	No	30 Minutes at 250°F
R 137-1C	20 %	Yes	Air Dried
R 137-1D	20 %	No	Air Dried
R 137-2A	50%	Yes	30 Minutes at 250°F
R 137-2B	50%	No	30 Minutes at 250°F
R 137-2C	50%	Yes	Air Dried
R 137-2D	50%	No	Air Dried
R 137-3A	80%	Yes	30 Minutes at 250°F
R 137-3B	80%	No	30 Minutes at 250°F
R 137-3C	80%	Yes	Air Dried
R 137-3D	80%	No	Air Dried

Table 3.6-3 and Table 3.6-4 show the results for a parallel set of specimens where the sol-gel was heat-cured at 250°F rather than air-dried. There was no significant difference in the crack growth patterns for these heat-cured specimens. The crack growth and percentage cohesive failure of the Turco® 5578 etched samples slightly improved as the concentration of the alkaline etching solution was increased from 20% to 80%. The average crack growth of all twelve samples was less than 0.25in after six weeks of testing.

Table 3.6-3: Wedge Test Results for Turco® 5578 Etched Ti-6Al-4V Samples with Air-Dried Sol-Gel Coatings

Processing Prior to Sol-Gel	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr	
R 137-1C 20 % Turco® 5578, HNO3 Desmut, Air Dried	0.70	0.07	0.10	0.10	0.13	0.13	0.13	95% co
R 137-1D 20 % Turco® 5578, No HNO3 Desmut, Air Dried	0.77	0.06	0.08	0.08	0.14	0.14	0.15	94% co
R 137-2C 50 % Turco® 5578, HNO3 Desmut, Air Dried	0.73	0.04	0.06	0.06	0.08	0.09	0.09	99% co
R 137-2D 50 % Turco® 5578, No HNO3 Desmut, Air Dried	0.74	0.06	0.08	0.08	0.12	0.12	0.13	97% co
R 137-3C 80 % Turco 5578®, HNO3 Desmut, Air Dried	0.73	0.02	0.03	0.03	0.03	0.03	0.03	100% co
R 137-3D 80 % Turco® 5578, No HNO3 Desmut, Air Dried	0.72	0.04	0.04	0.04	0.04	0.05	0.05	100% co

* co: cohesive failure within the adhesive layer

Heat-curing the applied Boegel-EPII coatings for 30 minutes at 250°F, rather than air-drying them before priming with BR 6747-1, produced relatively small differences in performance between the majority of the samples etched in 50% or 80% Turco® 5578. However, the performance of samples etched in the 20% Turco® solution were found to be somewhat dependent on the combinations of desmutting treatment and method of curing used.

Table 3.6-4: Wedge Test Results for Turco® 5578 Etched Ti-6Al-4V Samples with 250°F Heat-Cured Sol-Gel Coatings

Processing Prior to Sol-Gel	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr	
R 137-1A 20 % Turco® 5578, HNO3 Desmut, 30min @ 250°F	0.72	0.07	0.14	0.17	0.18	0.21	0.21	42% co
R 137-1B 20 % Turco® 5578, No HNO3 Desmut, 30min @ 250°F	0.70	0.06	0.08	0.10	0.10	0.10	0.10	97% co
R 137-2A 50 % Turco® 5578, HNO3 Desmut, 30min @ 250°F	0.72	0.02	0.07	0.07	0.10	0.10	0.10	98% co
R 137-2B 50 % Turco® 5578, No HNO3 Desmut, 30min @ 250°F	0.75	0.04	0.06	0.07	0.08	0.09	0.09	91% co
R 137-3A 80 % Turco® 5578, HNO3 Desmut, 30min @ 250°F	0.72	0.03	0.06	0.07	0.07	0.08	0.09	98% co
R 137-3B 80 % Turco® 5578, No HNO3 Desmut, 30min @ 250°F	0.72	0.04	0.05	0.05	0.10	0.10	0.11	99% co

* co: cohesive failure within the adhesive layer

For the samples etched in 20% Turco® 5578 solution, the 250°F curing of the applied Boegel-EPII coating produced negative effects on the failure modes for samples which had been desmutted in 35% HNO_3 at 140°F. Heat curing did not negatively affect the performance of the corresponding sample that had not been desmutted in the HNO_3 solution. Among the remaining samples etched in the 20% Turco® solution and air-dried after the application of Boegel-EPII, the differences in performance between samples that were desmutted or not were much smaller. Regardless of the Boegel-EPII coating curing method on the 20% Turco® 5578 conditioned substrates, desmutted samples had poorer failure modes than those that were not desmutted.

The performance differences between the samples in the R 137 series might be explained by the interaction between Boegel-EPII coatings and substrates with varied surface areas and morphologies. Surface profilometer and gloss meter measurements of the surfaces of Ti-6Al-4V witness panels etched in 20%, 50%, and 80% Turco® 5578 indicated that the surface roughness of the Turco®-conditioned panels increases with solution concentration. It is possible that, in addition to macroscopic roughness, morphological features or surface chemistry changes that have positive influences on the formation and maintenance of durable bonds might also be formed during the Turco® 5578 conditioning process.

The quality and characteristics of the surfaces produced by immersion in 50% or 80% Turco® 5578 solutions may be sufficient to compensate for limited reductions in Boegel-EPII coating effectiveness.

3.7 Laser Etching Pretreatment (General Lasertronics Corporation)

Laser etching was examined as an alternate "nonchemical" method for deoxidizing and activating the metal surface prior to sol-gel application. Three sets of Ti-6Al-4V wedge test adherends were laser etched at the General Lasertronics Corporation (GLC) facility using the GLC A600 laser. One pass of the laser over the surface (at approximately 0.42 ft^2/min) was used to treat the adherends. Afterward, the titanium surfaces were uniform and shiny in appearance with no evidence of residual oxidation or change in surface roughness. NADEP Cherry Point personnel applied Boegel-EP to the laser-etched surfaces by spraying with a hand-pump spray gun. Priming was also carried out using the hand-sprayer using Cytec BR 6747-1. This was the only type of spray equipment available at the site. The configuration is described in Table 3.7-1. Use of the hand-pump spray gun resulted in a relatively uneven primer coating thickness. The panels later bonded at Boeing using AF 163-2M adhesive and machined into wedge test specimens. Test results are presented in Table 3.7-2.

Table 3.7-1: Specimen Configuration for GLC Etch Study

Specimen #	Metal Substrate	Failure Mode (% cohesive)
D62-1	Ti-6Al-4V	0%
D62-2	Ti-6Al-4V	0%
D62-3	Ti-6Al-4V	0%

Table 3.7-2: Wedge Test Results for the GLC Etch Process

Lasertronics Processing	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr	
D62-1, Ti-6Al-4V	0.77	0.15	0.27	0.32	0.32	0.32	0.32	0% co
D62-2, Ti-6Al-4V	0.75	0.09	0.15	0.16	0.16	0.16	0.20	0% co
D62-3, Ti-6Al-4V	0.74	0.09	0.21	0.21	0.21	0.21	0.27	0% co

* co: cohesive failure mode within the adhesive layer

The failure modes were 100% adhesional at the sol-gel-to-metal interface on all Ti specimens (D62-1, 2, 3). Analysis of the specimens showed a close relation between the failure modes and the primer application. The primer was very thick in areas and uneven overall. Due to the poor priming process, it is likely the laser-etch process was not properly evaluated.

3.8 Sol-Gel Chemistries

3.8.1 Effect of Surfactants

A study was begun to understand the effect of adding surfactant to the Boegel-EPII solution for titanium bond performance. Addition of a surfactant to the aqueous-based sol-gel can improve the wettability of the sol-gel solution on titanium and result in a more uniform coating. This more uniform coating may (or may not) address the issue of the mixed mode failures that are typically observed with the sol-gel treatment of titanium. It has been routinely observed that, in a given wedge test, mixed mode failure are observed without substantial crack growth. In fact,

when the failure mode is driven to the metal surface, it does not continue to fail in an adhesional manner along this interface. It is postulated that (1) this may be an inherent method of failure for the sol-gel systems that may be related to the chemical bonding interaction versus the mechanical interlock or (2) an uneven coating is being deposited on the surface resulting in adhesional failure in areas where the metal is not coated sufficiently. The latter problem could theoretically be addressed by improving coating uniformity over the surface. The results of the surfactant testing using FC-170C from 3M Company are shown in Table 3.8-1.

Table 3.8-1: Influence of a Cationic Surfactant on Ti-6Al-4V Wedge Test Performance

Additives to Boegel-EPII	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr	
P 25-1 0.0250g FC-170C / Liter	0.78	0.00	0.03	0.04	0.11	0.11	0.13	100% co
P 25-2 0.0125g FC-170C / Liter	0.87	0.01	0.01	0.03	0.03	0.05	0.05	100% co
P 25-3 0.0062g FC-170C / Liter	0.79	0.01	0.08	0.08	0.10	0.10	0.14	100% co
No surfactant	0.68	0.10	0.10	0.11	0.12	0.13	0.13	100% co

* co: cohesive failure mode within the adhesive layer

3.8.2 Surfactant Evaluation

During the course of this project, 3M's FC-170C surfactant was discontinued along with the remainder of the 3M surfactant product line. Thus, the surfactant screening studies were rerun in an attempt to find a replacement that was adequate for improving the sol-gel coating uniformity, especially over smooth surfaces. To this regard, screening studies were performed on several new surfactant systems in Boegel-EPII on titanium surfaces pretreated with Turco® 5578. One surfactant in particular appeared to yield a relatively uniform coating. Thus, after initial appearance uniformity studies, wedge tests were performed using a product from CPS Chemical called Agesperse PA8405. This is an acrylic polymer in aqueous solution. The surfactant was added to serial dilutions of Boegel-EPII: full strength, ½, and ¼ strength. Normal sol-gel (sans surfactant) was also included as a control. The concentration of surfactant was 0.05 wt % in all solutions. The solutions were applied to Ti-6Al-4V that had been processed through a 20% Turco® tankline, primed with BR 6747-1, and bonded using AF 163-2M adhesive. Table 3.8-2 shows the wedge test performance at 3 weeks. None of the surfactants appeared to degrade the performance of the bondline.

Table 3.8-2: Effect of Adding 0.05 wt% Agesperse PA8405 Surfactant to Boegel-EPII Solution

Additives to Boegel-EPII	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
C52-1: 1/4 strength	0.75	0.08	0.11	0.11	0.14	80% co
C52-2: Full strength	0.75	0.06	0.09	0.09	0.14	88% co
C52-3: 1/2 strength	0.79	0.05	0.05	0.05	0.07	98% co
C52-4: control	0.74	0.07	0.10	0.10	0.14	81% co

* co: cohesive failure mode within the adhesive layer

3.9 Primer Evaluations

3.9.1 Manual Primer Application

Three versions of Cytec BR 6747-1 primer were used for a foam brush application study on alumina grit-blasted, Scotch-Brite™ Roloc™ disc abraded, and #220 alumina hand abraded Ti-6Al-4V panels using a foam brush. The three versions differed by the solids content: 20%, 30%, and 50% solids. The 50% solid primer brushed on very nicely, giving a uniform coating. The cured coating thicknesses for the various substrates are listed in Table 3.9-1. All panels received only one brush pass of primer. The wedge tests results for the Cytec BR 6747-1 50% solids brushed-on primer over Ti-6Al-4V (C79-1) are shown in Table 3.9-2.

Table 3.9-1: Cytec BR6747-1 Primer Thickness

Panel	Surface Prep	BR 6747-1 Primer - % Solids	Average Primer Thickness (mils)
C79-1	#180 grit-blast	50	0.20
C79-2	#180 grit-blast	50	0.35
C79-3	#220 sanded	20	0.01
C79-3	#220 sanded	30	0.05
C79-3	#220 sanded	50	0.28
C79-4	Roloc™ abraded	20	0.03
C79-4	Roloc™ abraded	30	0.01
C79-4	Roloc™ abraded	50	0.43

Table 3.9-2: Ti-6Al-4V Wedge Test Results with Cytec BR 6747-1 Primer (50% Solids)

Bond Process	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr	
C79-1; #180 grit blast, brush-on primer	0.74	0.05	0.09	0.09	0.09	0.11	0.12	95% co

* co: cohesive failure mode within the adhesive layer

3.9.2 Cocuring Primer and Adhesive

An evaluation was conducted to examine the effect of cocuring the primer and adhesive using grit-blast deoxidation of the titanium substrate prior to application of the sol-gel solution. Two sets of samples were prepared at different times, months apart. Wedge test and peel adherends were grit-blasted followed by Boegel-EPII application. After the sol-gel had dried for about 30 minutes at ambient conditions, adherends were primed with BR 6747-1 to a thickness of 0.1-0.3 mil. The primer was dried at ambient conditions for about 30 minutes, and the panels were then immediately laid up with AF 163-2K film adhesive. Primer and adhesive were cocured at 250°F under 40 psi for 60 minutes. Wedge test specimens were tested at 140°F and 95-100% RH. Results are shown in Table 3.9-3. Floating roller peel results, tested dry and wet, are shown in Table 3.9-4. These data show that the grit-blast cocure process gives good results, with the titanium substrate showing low crack growth. Both sets exhibited a high level of cohesive failure indicating that cocuring the adhesive and primer is a viable option for grit-blasted titanium substrates.

Table 3.9-3: Wedge Test Results for Ti-6Al-4V with Cocured Primer and Adhesive

Treatment	Initial	Cumulative Crack Growth (in)									
	(in)	1 hr	4 hr	8 hr	24 hr	48 hr	7 days	14 days	21 days	28 days	56 days
Grit Blast Cocure 1	0.76	0.00	-	-	0.04	-	0.09	0.10	0.10	0.12	-
Grit Blast Cocure 2	0.68	0.01	0.08	0.12	0.14	0.14	0.15	0.16	0.16	0.17	0.18

Table 3.9-4: Floating Roller Peel Results for Ti-6Al-4V with Cocured Primer and Adhesive

	RT (»70°F) Test	DI Water Squirt Test at RT
Peel Strength (lb/in)	50.7	48.3
Standard Deviation	5.3	2.1

3.10 Alternate Adhesive Data

3.10.1 Testing with Cytec Metlbond 1515 Adhesive

Sets of wedge test, climbing drum peel, flatwise tensile, and lap shear specimens were fabricated from Ti-6Al-4V alloy. The specimens were cleaned, etched in HF/HNO_3, and treated with 20% Turco® 5578, followed by a nitric acid desmut. The specimens were then sprayed with Boegel-EP (an older, lower pH version of Boegel-EPII), primed with Cytec BR 6747-1 primer, and bonded with Cytec Metlbond 1515, 0.05psf adhesive. This particular adhesive system was chosen due to its use in titanium honeycomb structures. These specimens were actually coated with an older, higher-acid content version of the sol-gel that was used for bonding. The wedge crack extension data are shown in Table 3.10-1. The data shown are the average for 3 of the 5 specimens over 1000 hours. Two specimens from the panel set were removed at 30 days to determine the failure modes. The specimens removed at 30 days showed 0% cohesive failure and 40% cohesive failure. The three specimens tested for 1000 hours all had adhesional failure, with some at the primer to adhesive interface. No surface analyses were conducted to determine the exact mode of interfacial failure.

The climbing drum peel results are illustrated in Table 3.10-2. The values are comparable to those achieved with similar 350°F-cure adhesives.

Table 3.10-1: Ti-6Al-4V Sol-Gel Wedge Test Results Using Metlbond 1515 Adhesive

Bond Process	Initial	Cumulative Crack Growth (in)						Failure
	(in)	24hr	168hr	336hr	504hr	672hr	1008hr	Mode*
HF/HNO3/ Turco® 5578/desmut/sol-gel/BR 6747-1/Metlbond 1515	1.14	0.03	0.03	0.08	0.09	0.14	0.14	25% co

* co: cohesive failure within the adhesive layer

Table 3.10-2: Ti-6Al-4V Climbing Drum Peel Results Using Metlbond 1515 Adhesive

	Peel Strength (lb/in)	Failure Mode (% cohesive)
Room Temp (»70°F)	6.5	33%
-65°F	4.1	5%

The flatwise tension test results are given in Table 3.10-3, and the lap shear results are shown in Table 3.10-4.

Table 3.10-3: Flatwise Tension Results (Ti Honeycomb Core Specimens)Using Metlbond1515

Specimen	Test Temp (°F)	Average Tensile Strength (psi)
R103-1	70 (RT)	1180
R103-6	-65	1273
R103-11	160	997
R103-16	160 wet	998

Table 3.10-4: Ti-6Al-4V Lap Shear Results Using Metlbond 1515

Specimen No.	Test Temp (°F)	Average Strength (psi)
R103-1	70 (RT)	3044.6
R104-1	-65	2984.0
R105-1	180	2647.6

3.10.2 *Compatibility with AF 191 350°F Adhesive*

The compatibility of a 350°F-cure epoxy adhesives with the sol-gel surface preparation was evaluated. Wedge test performance for sol-gel on titanium using 3M Company AF 191, in comparison with the 250°F system, is shown in Table 3.10-5. The failure mode was 100% cohesive. These specimens exhibited very small crack extension (0.02 inch). However, the initial crack is slightly longer for the 350°F system.

Table 3.10-5: Wedge Test Results Comparing 3M's AF 191 and AF 163-2 Adhesives for Sol-Gel Treatment of Ti-6Al-4V

Bond Process	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr	
HF/HNO3/ Turco® 5578/desmut/sol-gel BR6 747-1/AF 191	0.90	0.01	0.02	0.02	0.02	0.02	0.02	100% co
HF/HNO3/ Turco® 5578/desmut/sol-gel BR 6747-1/AF 163-2M	0.76	0.03	0.04	0.05	0.05	0.06	0.06	100% co

* co: cohesive failure within the adhesive layer

3.10.3 Compatibility with FM 300 350°F Adhesive

An additional wedge test was performed using another 350°F cure adhesive, Cytec FM 300. Grit-blast deoxidation was used prior to the application of the sol-gel solution. BR 6747-1 primer was applied to a film thickness of 0.1-0.3 mil and cured at 250°F for 60 minutes after a 30-minute ambient dry. The panels were bonded with FM-300 film adhesive and cured at 350°F

under 40 psi for 60 minutes. Wedge test specimens were conditioned at 140°F and 95-100% RH. Results are shown in Table 3.10-6 below. The results are excellent, with very small crack growth and failure modes that were 100% cohesive.

Table 3.10-6: Wedge Test Results on Ti-6Al-4V Using Cytec FM 300 Adhesive

Adhesive	Initial	Cumulative Crack Growth (in)									
	(in)	1 hr	4 hr	8 hr	24 hr	48 hr	7 days	14 days	21 days	28 days	56 days
FM-300	0.95	0.01	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.03

4 ADHESIVE BONDING - STEEL SUBSTRATES

Surface preparation of steel alloys typically requires the use of strong chemical etches. The use of Boegel-EPII has the potential to significantly reduce the use of hazardous chemicals in these surface preparation processes. The feasibility of forming durable adhesive bonds with steel and nickel-based alloys has been demonstrated with this sol-gel technology. In this project, the steel treatment effort focused primarily on stainless steel alloy applications for both OEM and repair environments. Grit-blast/sol-gel using Boegel-EPII produces results that are equal to or better than the baseline OEM ferric chloride-hydrochloric acid etch (FCHAE) process.

4.1 Testing and Materials

A number of materials and processes were evaluated during this effort. In most cases, the details for the processing associated with the evaluations are given for each test. At times, full details for parameters held constant are not provided. Unless otherwise noted, test results are the average of 5 specimens taken from one bonded AM355 or 301 stainless steel panel. Since AM355 alloy is very difficult to obtain, 301 stainless steel was often used for screening purposes. Grit-blasting was performed using 80 micron (#180) or 98 micron (#150) alumina. "Sanding" processes employed SiC abrasive paper. The sol-gel formulations evaluated include the basic Boegel-EPII and Fe 9552, a mixture of Chemat's Al 9201 and Cytec BR 6747-1 primer. Treated surfaces were kept wet with the sol-gel solutions for 2-3 minutes. Cytec BR 6747-1 waterborne, chromated bond primer (20% solids) was used when a separate priming step was required. For baseline specimens, the primer was applied via spray gun to a nominal thickness of 0.1-0.3 mil (0.0001-0.0003 inch), dried for 30 minutes at ambient temperature, and cured for 60 minutes at 250°F in an air-circulating oven. However, some primer-adhesive cocure specimens were included for some cases. Baseline specimens were bonded with 3M Company AF 163-2M (0.06psf) modified epoxy film adhesive that was autoclave cured for 60 minutes at 250°F under 35-45 psi. In some cases, the one-side tacky (OST) version of the adhesive was used, but this is not separately noted. Additional adhesives related to Army rotorcraft applications were evaluated, including Cytec FM 94 (production) and Cytec FM 300-2K (repair). The wedge test was conducted at 140°F.

4.2 Baseline Testing

A sample set of 301 stainless steel alloy was procured for screening testing. Selected physical property data for several aerospace stainless and alloy steels are shown in Table 4.2-1. While differences in alloy chemistry will affect methodologies for activating and treating the steel surfaces, general information should be obtainable by using the 301 steel for screening-level tests.

Baseline wedge test data developed by the Army for existing processes are shown in Table 4.2-2. Cytec's BR 127 solventborne, chromate-containing primer was evaluated with 3M's AF 163-2K modified epoxy film adhesive on the production baseline FCHAE panels. AF 163-2K was used without a primer on the repair baseline silane-treated surfaces and Chemat Fe 9552 sol-gel-treated surfaces. The silane used was Dow Corning Z-6040 (γ-glycyidoxypropyltrimethoxy silane) hydrolyzed in water and applied over a grit-blasted surface.

Table 4.2-1: Selected Physical Property Data for Several Stainless and Alloy Steels[28]

Property	AM 355	301	316	4340
Composition	C 0.10, Mn 0.95, Si 0.25, Cr 15.5, Ni 4.3, Mo 2.8, N 0.10, Fe bal	C 0.15, Mn 2, Si 1, P 0.045, S 0.03, Cr 16-18, Ni 6-8, Fe bal	C 0.08, Mn 2, P 0.045, S 0.030, Si, 1.0, Cr 16-18, Ni 10-14, Mo 2-3, Fe bal	C 0.40, Mn 0.85, Si 0.20, Cr 0.75, Ni 1.8, Mo 0.25, Fe bal
Density, lbs/in^3	0.282	0.29	0.29	0.283
Thermal Conductivity, 212°F, Btu-ft/hr-ft^2-°F	9.2	9.4	9.4	
Electrical Resistivity, microohm-cm	76	72	74	
Corrosion Resistance	very good atmosphere resistance	very good atmosphere resistance	Excellent	
Tensile Strength, 10^3 psi annealed	186	110 (sheet)	84	287

Table 4.2-2: Wedge Test Performance Data for Baseline Processes on Stainless AM355 (0.040in-thick) Specimens

Surface Preparation Process	Initial (in)	Cumulative Crack Growth (in)				
		1hr	8hr	24hr	72hr	168hr
Baseline $FeCl_3$/HCl Etch (FCHAE)	0.40	0.95	1.05	1.10	1.10	1.10
Grit-blast/Z-6040 Silane	0.50	0.18	0.28	0.34	0.58	0.60

Neither of the two baseline processes performed well in the wedge test. The ferric chloride process has since been upgraded by adding a grit-blast pretreatment step. This change dramatically increased the hot/wet performance of the FCHAE surface treatment.

4.3 Initial 301 Stainless Steel Testing

Initial feasibility tests were performed using the existing Boegel-EPII formulation and process conditions used for aluminum to see what type of bond performance and durability this system will yield on a stainless steel substrate. Adherends sized 6 inch x 6 inch x 0.040 inch were used for this test. The adherends were grit-blasted with #180 alumina grit and spray-drenched with the Boegel-EPII solution. Treated adherends were primed with Cytec BR 6747-1 primer and bonded with AF163-2M adhesive. Initial wedge test performance is shown in Table 4.3-1. Controls include both the original FCHAE and the improved grit-blast version of the FCHAE.

Table 4.3-1: Wedge Test Performance Comparing Surface Treatments on Stainless 301 Bonded with 3M AF163-2M Adhesive

Surface Preparation Process	Initial (in)	Cumulative Crack Growth (in)				
		24 hr	168 hr	336 hr	504 hr	672 hr
Original FCHAE Treatment	0.67	0.55	0.71	0.77	0.77	0.77
Modified Grit-blast/FCHAE Treatment	0.57	0.18	0.23	0.23	0.23	0.25
#180 Alumina Grit Blasted, Spray-Drench Coated with Boegel-EPII	0.64	0.02	0.04	0.04	0.04	0.04

Lap shear and peel test specimens were also prepared. Lap shear test results for 0.040in-thick, ½ hard 301 stainless steel substrates are reported in Table 4.3-2. These specimens were grit-blasted with #180 alumina grit, spray-drench coated with Boegel-EPII, primed with BR 6747-1, and bonded with AF 163-2M. Lap shear data are indicative of the adhesive strength. Failure modes for the lap shear specimens were 100% cohesive. Climbing drum peel test results for 0.040in-thick, ½ hard 301 stainless steel substrates are reported in Table 4.3-3.

Table 4.3-2: Lap Shear Results for 301 Stainless Bonded with AF 163-2M

Grit Blast / Sol-Gel / BR 6747-1	Lap Shear Strength (psi)	Failure Mode (% co)
-67°F	8158	100%
Room Temperature (≈70°F)	6058	100%
180°F	3654	100%

co: cohesive failure within the adhesive layer

Table 4.3-3: Climbing Drum Peel Results for 301 Stainless Bonded with AF163-2M

Grit-blast / Sol-Gel / BR 6747-1	Peel Strength (pli)	Failure Mode (% co)
Room Temperature	61.6	100%

4.4 301 Stainless Steel - Repair Environment Testing

Two sets of 301 stainless steel wedge test specimens (Army 0301-1 and Army 0101-2) were fabricated to compare the standard grit-blast/silane repair process to the grit-blast/sol-gel procedure. The grit-blast/silane panels were blasted with #150 aluminum oxide grit, spray-coated with silane, spray-primed with Cytec BR 127 solventborne primer, and bonded with Cytec FM 300-2K film adhesive. The grit-blast/sol-gel panels were blasted with 150-grit aluminum oxide, spray-coated with Boegel-EPII, spray-primed with Cytec BR 6747-1 waterborne primer and bonded with FM 300-2K. The 28-day data generated at 180°F and 95% RH (test conditions requested by the Army) are displayed in Table 4.4-1. The crack extension for the grit-blast/silane specimens was over 3 times greater than that for the grit-blast/sol-gel specimens. Failure mode measurements were in favor of the grit-blast/sol-gel specimens as well. In this iteration, grit-blast/sol-gel exhibited superior performance over grit-blast/silane when exposed to these severe conditions (180°F and 95% RH).

Table 4.4-1: Grit-Blast/Silane vs. Grit-Blast/Sol-Gel Wedge Test Results for 301 Stainless Steel

Surface Preparation	Initial Crack Length (in)	28-day Crack Extension (in)	Total Crack Length (in)	Failure Mode (% cohesive)
Grit-blast/silane (Army 0301-1)	0.831	0.286	1.117	33
Grit-blast/sol-gel (Army 0101-2)	0.775	0.090	0.865	70

4.5 Initial AM355 Stainless Steel Testing

Wedge test and lap shear specimens were fabricated from AM355 steel. The substrates were grit-blasted, treated with Boegel-EPII, primed with Cytec BR6747-1, and bonded with AF163-2M adhesive. Unfortunately, the wedge test and peel specimens were badly burnt during the machine-cutting step, so all testing results were nullified. The lap shear results are shown in Table 4.5-1. The mode of failure at both testing temperatures was cohesive.

Table 4.5-1: Lap Shear Results for AM355 Steel Specimens B66-L

AM355 /Grit Blast / Sol-Gel / BR 6747-1	Lap Shear Strength (psi)	Failure Mode (% co)
-65°F	7750	100%
Room Temperature (≈70°F)	6810	100%
co: cohesive failure within the adhesive layer		

Wedge test specimens were fabricated a second time from AM355 steel. The substrates were grit-blasted, treated with Boegel-EPII, primed with Cytec BR6747-1, and bonded with AF163-2M adhesive. The wedge test results for conditioning at 140°F and 95-100% RH are shown in Table 4.5-2. The failure modes were 95% cohesive failure with the small amount of adhesional failure found at the edges of the specimens, which were burned during machining. Some failure was observed between the primer and the adhesive, which most likely occurred during the forced opening of the specimens during the failure analysis.

Table 4.5-2: Total Crack Length for AM355 Specimens

Surface Preparation Process	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr	
#180 Alumina Grit Blasted, Boegel-EPII Coated	0.64	0.02	0.04	0.04	0.04	0.04	0.05	95% co

* co: cohesive failure within the adhesive layer

4.6 AM355 Stainless Steel - OEM Environment Testing

Four sets of AM355 stainless steel wedge test specimens (Army 0101-3, 0101-4, 0101-5, 0101-6) were fabricated to compare the grit-blast/sol-gel process with precured primer to the grit-blast/sol-gel process with cocured primer and adhesive. All four sets were grit blasted with 150-grit aluminum oxide, spray-coated with Boegel-EPII, and spray-primed with Cytec BR 6747-1. The primer was precured for two sets of panels and cocured with the film adhesive for the other two sets of panels. Two adhesives were used: 3M Company AF 163-2M and Cytec FM 94. The 28-day results generated at 140°F and 95% RH are displayed in Table 4.6-1. Precure and cocure results for both adhesives were comparable and generally exhibited excellent crack extension and failure mode values. The cocure process appeared to provide an advantage when used with FM 94 adhesive, but additional tests will have to be conducted to verify this result.

Table 4.6-1: Grit-Blast/Sol-Gel Wedge Test Results for AM355, Precure vs. Cocure

Specimen Set	Primer Cure	Adhesive	Initial Crack Length (in)	Total Crack Extension (in)	Total Crack Length (in)	Failure Mode (% cohesive)
Army 0101-3	Precure	AF 163-2M	0.62	0.08	0.70	99
Army 0101-4	Cocure	AF 163-2M	0.62	0.10	0.72	96
Army 0101-5	Precure	FM 94	0.66	0.11	0.77	90
Army 0101-6	Cocure	FM 94	0.65	0.08	0.73	99

4.7 Alternative Manual Deoxidation Techniques

Wedge tests (140°F and 95-100% RH) were conducted using 301 stainless steel in an attempt to identify an adequate nongrit-blast manual deoxidation treatment. Results for a "sanding" approach are compared to grit-blast in Table 4.7-1. The R41-2 samples were prepared by sanding each panel a total of four times, for 30 seconds each, using two pieces of #400 SiC paper followed by two pieces of #220 SiC paper. The crack growth for these samples was about 0.15 inch greater than that for the grit-blasted samples.

Table 4.7-1: Wedge Test Results for 0.040in-thick 301 Stainless Steel with Sanding Pretreatment

Processing Prior to Sol-Gel	Initial (in)	Crack Growth (in)					
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr
R 41-1: #180 Alumina Grit Blasted	0.64	0.02	0.04	0.04	0.04	0.04	0.05
R 41-2: Sanded Twice with 2 Pieces of #400 SiC Paper and Twice with 2 Pieces #220 SiC Paper, 30 seconds Sanding per Piece	0.70	0.03	0.16	0.16	0.16	0.18	0.19

4.8 Optimized Grit-blast/Sol-gel Process for Stainless Steel

The optimized grit-blast/sol-gel process for stainless steel is similar to that for aluminum alloys. Table 4.8-1 shows the Army wedge test verification data for that process on 301 stainless specimens bonded with AF 163-2M adhesive. It included blasting with #150 alumina after solvent cleaning with MEK. Blasting debris was removed dry, without the use of solvents. The simplified Boegel-EPII mix procedure was used (described in Section 5.6). The sol-gel solution was spray applied (Binks Mach 1SL HVLP gun), and the surface was kept wet with solution for 2.5 minutes. After a 60-minute dry at ambient conditions, BR 6747-1 primer was spray applied and procured prior to adhesive application. The results show the process on stainless alloys yielded excellent crack growth and failure mode results for conditioning at 140°F and >98% RH.

Table 4.8-1: Wedge Test Results for Optimized Grit-Blast/Sol-Gel on 301 Stainless Steel

Surface Preparation Process	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		8hr	24hr	168hr	336hr	504hr	672hr	
Optimized Grit-blast/Sol-gel	0.57	0.03	0.07	0.07	0.08	0.08	0.08	96% co

* co: cohesive failure within the adhesive layer

5 KITTING

The purpose of this task is to make the sol-gel process more user-friendly. For current hardware applications, a rudimentary kitting system was developed that worked quite well for laboratory operations. The sol-gel components were packaged in high-density polyethylene or polypropylene syringes with plastic caps and sealed to prevent ingression of air and moisture. This kitting concept is shown in Figure 5.0-1.

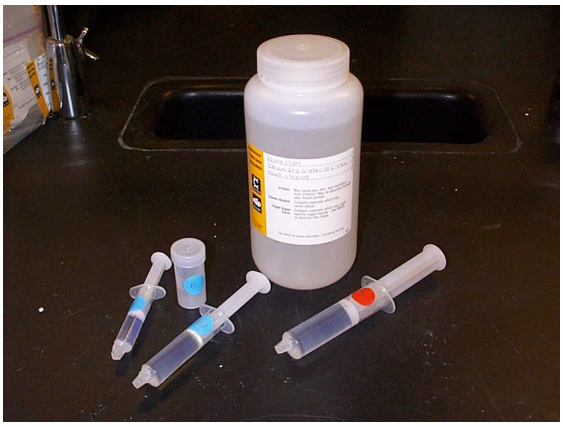


Figure 5.0-1: Rudimentary Kitting Concept for Sol-Gel Components

A goal of the testing for this program was to limit the number of components in the kit to simplify the deployment, especially for field-use conditions. Currently, there are four separate components in the sol-gel kits: γ-glycidoxypropyltrimethoxysilane (GTMS), zirconium n-propoxide (TPOZ), glacial acetic acid GAA), and water. Testing indicates that precombining the GAA and TPOZ components provides a stable mixture that gives good performance results for kits aged up to one year. Additionally, combining the GAA, TPOZ, and water could reduce the number of kit components even further. This mixture of three chemicals also gave acceptable results in kits aged for one year. This latter premixed kit would present the most ideal situation, as only two components would be involved in the sol-gel kit. The FC-170C surfactant was included in the kit studies, although it is no longer available and is not present in existing four-part commercial kits (AC Tech's AC-130). During the kit studies, a small amount of isopropyl alcohol (IPA) was added to determine if it would extend shelf life. Commercially available kits do not contain IPA. Verification of the initial testing using the commercial sol-gel supplier (AC Tech) is required before carrying out any change in the kit configuration. Improved packaging concepts will be identified by the supplier and tested for shelf stability.

5.1 Kit Specifications

Kits should be clearly labeled with concise mixing instructions and chemical hazard warnings. The containers should be either high-density polyethylene (HDPE) or polypropylene (PP) or a similar nonreactive material to prevent attack by the chemicals, leakage, and breakage during shipping and use. Certain reagents used in the sol-gel formulation are sensitive to moisture. The color and/or presence of precipitates can indicate whether the chemicals in the kit are viable after a certain shelf life. Therefore, the containers should be clear or translucent so the physical

appearance of the liquid can be easily determined. To make the mixing process as easy as possible, kits should use a mixing procedure using terminology similar to that used in mixing multi-part paint kits. The sol-gel solution will be sprayed, swabbed, or brushed onto the substrate, so it may be desirable for the kit to contain the necessary materials for the application procedure.

Ideally, the kit should contain a minimum number of components in order to reduce the amount of mixing and limit exposure to the chemicals. It is particularly desirable to limit exposure to GAA, possibly through premixing with TPOZ. Water and surfactant, if used, should be combined in the kit, as the amount of surfactant used in the formulation is extremely small. Kits should have a minimum shelf life of one year.

5.2 First-Generation Kit Studies

Screening tests were conducted to ascertain how the sol-gel chemical components would survive over an identified shelf life when packaged in appropriate vessels. Initial kitting studies were performed on #180 alumina grit-blasted Al 2024-T3 surfaces. Parallel to the performance verification effort, the individual candidate kit components were characterized by FTIR. Each component combination was tested by infrared spectroscopy at various aging times to determine its stability over time.

The test matrix in Table 5.2-1 was followed. The various combinations were premixed and stored in containers at ambient conditions for 4 weeks, 7 weeks, 6 months, and 12 months. At the specified time, the sol-gel test formulation was mixed using the appropriate test components and applied to a set of grit-blasted Al 2024-T3 adherends which were primed with BR 6747-1 (precured) and bonded with AF 163-2M adhesive. The control specimens contain no premixed components.

Wedge tests were conducted to assess the adhesive-bonded surface durability. Selection criteria were based on the historical database of performance for the grit-blasted Boegel-EPII specimens and how they compare to specimens prepared using phosphoric acid anodize treated panels.

5.2.1 Four-Week Old Kits

As shown in Table 5.2-2, two specimens exhibited average crack growth greater than 0.25 inch after 500 hours of exposure to 140°F and >95%RH. These specimens, I4-1-1 and I5-1-1, yielded crack extensions of 0.9 and 0.91 inch, respectively. They were the only combinations that included the premixing of water and GTMS. It was concluded that combining GTMS and water in a kit causes the condensation reaction to take place with the sol-gel components long before the mixture is applied to the substrate. The initiation of the condensation reaction, resulting in formation of a polymer before application to the substrate, results in poor adhesion and bonding performance. This is due to the lack of open attachment sites on the polymeric chain. The longer GTMS and water are in contact, the further the reaction will proceed and the fewer available sites for attachment to the metal substrate. The resultant degradation in bonding performance is exhibited by large crack extensions. It was concluded that water and GTMS should be kept separate in the sol-gel kit.

Specimens I2-1, containing a premixed combination of deionized water and FC-170C surfactant, exhibited crack growth similar to the controls. A preliminary conclusion was made that a sol-gel kit containing deionized water mixed with FC-170C surfactant was acceptable.

Table 5.2-1: Kitting Chemical Compatibility Matrix

TEST CATEGORY	TEST	TEST LABEL	4 WKS	6WKS	7 MONTHS	12 MONTHS
ALL COMPONENTS	Control					
	1. H2O					
	2. FC-170C					
	3. GTMS					
	4. GAA					
	5. IPA		A1-1-1		A1-3-1	
	6. TPOZ	A1	A1-1-2		A1-3-2	
	1. H2O					
	2. FC-170C					
	3. GTMS		A2-1-1	A2-2-1	A2-3-1	A2-4-1
	4. GAA + TPOZ + IPA	A2	A2-1-2	A2-2-2	A2-3-2	A2-4-2
	1. H2O					
	2. FC-170C					
	3. GTMS + TPOZ + IPA		A3-1-1	A3-2-1	A3-3-1	A3-4-1
	4. GAA	A3	A3-1-2	A3-2-2	A3-3-2	A3-4-2
W/OUT SURFACTANT	Control					
	1. H2O					
	2. GTMS					
	3. GAA					
	4. IPA		S1-1-1		S1-3-1	
	5. TPOZ	S1	S1-1-2		S1-3-2	
	1. H2O					
	2. GTMS					
	3. GAA		S2-1-1	S2-2-1	S2-3-1	S2-4-1
	4. TPOZ + IPA	S2	S2-1-2	S2-2-2	S2-3-2	S2-4-2
	1. H2O					
	2. GTMS + TPOZ					
	3. GAA		S3-1-1	S3-2-1	S3-3-1	S3-4-1
	4. IPA	S3	S3-1-2	S3-2-2	S3-3-2	S3-4-2
W/OUT IPA	Control					
	1. H2O					
	2. FC-170C					
	3. GTMS					
	4. GAA		I1-1-1		I1-3-1	
	5. TPOZ	I1	I1-1-2		I1-3-2	
	1. H2O + FC-170C					
	2. GTMS					
	3. GAA		I2-1-1	I2-2-1	I2-3-1	I2-4-1
	4. TPOZ	I2	I2-1-2	I2-2-2	I2-3-2	I2-4-2
	1. H2O					
	2. GTMS + FC-170C					
	3. GAA		I3-1-1	I3-2-1	I3-3-1	I3-4-1
	4. TPOZ	I3	I3-1-2	I3-2-2	I3-3-2	I3-4-2

Table 5.2-1: Kitting Chemical Compatibility Matrix, Continued

TEST CATEGORY	TEST	TEST LABEL	4 WEEKS	7 WEEKS	6 MONTHS	12 MONTHS
W/OUT IPA						
	1. H2O + GTMS					
	2. FC-170C					
	3. GAA		I4-1-1	I4-2-1	I4-3-1	I4-4-1
	4. TPOZ	I4	I4-1-2	I4-2-2	I4-3-2	I4-4-2
	1. H2O + GTMS + FC-170C					
	2. GAA		I5-1-1	I5-2-1	I5-3-1	I5-4-1
	3. TPOZ	I5	I5-1-2	I5-2-2	I5-3-2	I5-4-2
	1. H2O					
	2. FC-170C					
	3. GTMS		I6-1-1	I6-2-1	I6-3-1	I6-4-1
	4. GAA + TPOZ	I6	I6-1-2	I6-2-2	I6-3-2	I6-4-2
	1. H2O					
	2. FC-170C					
	3. GTMS + TPOZ		I7-1-1	I7-2-1	I7-3-1	I7-4-1
	4. GAA	I7	I7-1-2	I7-2-2	I7-3-2	I7-4-2
	1. H2O					
	2. GTMS + TPOZ + FC-170C		I8-1-1	I8-2-1	I8-2-1	I8-4-1
	3. GAA	I8	I8-1-2	I8-2-2	I8-3-2	I8-4-2
	1. TAP H2O					
	2. FC-170C					
	3. GTMS					
	4. GAA		I9-1-1	I9-2-1	I9-3-1	I9-4-1
	5. TPOZ	I9	I9-1-2	I9-2-2	I9-3-2	I9-4-2
W/OUT SURFACTANT OR IPA	Control					
	1. H2O					
	2. GTMS					
	3. GAA		SI1-1-1		SI1-3-1	
	4. TPOZ	SI1	SI1-1-2		SI1-3-2	
	1. H2O					
	2. GTMS		SI2-1-1	SI2-2-1	SI2-3-1	SI2-4-1
	3. GAA + TPOZ	SI2	SI2-1-2	SI2-2-2	SI2-3-2	SI2-4-2

Table 5.2-2: Wedge Test Results for 4-Week Old Sol-Gel Kit Trials

Kitting Conditions	**Initial (in)**	**Cumulative Crack Growth (in)**			
		24 hr	**168 hr**	**336 hr**	**504 hr**
RI1: Control, no premixing of components	1.26	0.10	0.15	0.15	0.15
I2-1: H2O + FC-170Ccombined prior to preparation	1.36	0.03	0.04	0.04	0.04
I3-1: GTMS + FC-170C combined prior to preparation	1.29	0.04	0.16	0.16	0.16
I4-1: H2O + GTMS combined prior to preparation	1.30	0.19	0.58	0.81	0.90
I5-1: H2O + GTMS + FC-170C combined prior to preparation	1.30	0.31	0.60	0.71	0.90
I6-1: GAA + TPOZ combined prior to preparation	1.30	0.12	0.14	0.14	0.14
I7-1: GTMS + TPOZ combined prior to preparation	1.26	0.09	0.13	0.16	0.17
I8-1: GTMS + TPOZ + FC-170C combined prior to preparation	1.27	0.04	0.13	0.17	0.17
I9-1: City of Kent Tap Water (Instead of DI H2O)	1.25	0.06	0.11	0.11	0.13

The crack growths for all wedge test specimens in this study were less than 0.25 inch, except for those fabricated using kits with premixed water and GTMS (I4-1 and I5-1). As shown in Table 5.2-2, the use of City of Kent tap water rather than deionized water, I9-1, did not degrade the performance of the specimen. However, the pH and contamination levels of tap water vary widely across the world and are difficult to control. It was determined that the water component would be included as part of the kit and would be deionized, in order to maintain control over the variable pH and contamination.

Wedge test behavior of IPA-containing specimens is shown in Table 5.2-3. The crack extensions for specimens containing a premixture of TPOZ and IPA continued to increase over the 500 hours of exposure. The premixed GTMS and TPOZ showed crack extensions similar to that of the control, with a larger initial crack length. As shown in Table 5.2-4, the specimens prepared with all components (including IPA and FC-170C) followed a similar trend as the control, but the difference in the total crack lengths is slightly larger than that for the other studies.

Table 5.2-3: Wedge Test Results for a 4-Week Aged Sol-Gel Kit with IPA Added

Sample Condition	**Initial (in)**	**Cumulative Crack Growth (in)**			
		24hr	**168hr**	**336hr**	**504hr**
S2-1: TPOZ + IPA combined prior to preparation	1.37	0.00	0.02	0.04	0.05
S3-1: GTMS + TPOZ combined prior to preparation	1.31	0.12	0.16	0.16	0.16
RS1: Control, no pre-mixing of components	1.22	0.10	0.12	0.12	0.12

Table 5.2-4: Wedge Test Results for a 4-Week Aged Sol-Gel Kit with All Components

Sample Condition	Initial (in)	Cumulative Crack Growth (in)			
		24hr	168hr	336hr	504hr
A2-1: GAA + TPOZ + IPA combined prior to preparation	1.34	0.09	0.15	0.15	0.15
A3-1: GTMS + TPOZ + IPA combined prior to preparation	1.30	0.11	0.15	0.15	0.17
RA1: Control, no pre-mixing of components	1.24	0.08	0.08	0.09	0.09

One of the biggest payoffs can occur if the TPOZ and GAA can be premixed in the kit. As previously mentioned, this would limit the number of components and minimize any exposure to acid components in the kit. As illustrated in Table 5.2-5, the sample prepared with a premixture of GAA and TPOZ had a total crack length trend similar to that of the control, with a slightly larger initial crack length. Further testing will show whether these premixtures will continue to yield acceptable results as the shelf life of the premixed components increases.

Table 5.2-5: Wedge Test for a 4-Week Aged Sol-Gel Kit with Premixed TPOZ and GAA

Sample Condition	Initial (in)	Cumulative Crack Growth (in)			
		24hr	168hr	336hr	504hr
SI2-1: GAA + TPOZ combined prior to preparation	1.28	0.04	0.13	0.13	0.13
RSI1: Control, no pre-mixing of components	1.21	0.12	0.16	0.16	0.16

Preliminary results indicate that several options may be acceptable for a sol-gel kit. Further testing is being performed to ensure the shelf life of these material combinations is adequate to meet the requirements of depot and field repair.

5.2.2 Seven-Week Old Kits

Wedge test results from application of the 7-week-old kits (Trial 2) on aluminum were evaluated. Specimens I4 and I5, containing a combination of GTMS and deionized water, were dropped from the matrix due to poor performance after 4-week aging. Specimens I9 were not tested after a 7-week shelf life since they were made by simply substituting tap water for deionized water. Specimens from A2 and A3 are not included in this trial due to mislabeling, but were included in Trials 3 and 4 (6 and 12 month shelf lives). The average crack extensions for the samples tested in this trial are shown in Table 5.2-6, Table 5.2-7, and Table 5.2-8. The failure modes for all of these specimens were predominantly cohesive (>90% cohesive within the adhesive layer).

Table 5.2-6: Wedge Test Results for Sol-Gel Panels Prepared with 7-Week-Old Kits with Premixed Components

Sample Condition	Initial (in)	Cumulative Crack Growth (in)			
		24hr	168hr	336hr	504hr
RI1: Control, no premixing of components	1.26	0.10	0.15	0.15	0.15
I2-2: H20 + FC-170C combined prior to preparation	1.27	0.04	0.15	0.16	0.17
I3-2A: GTMS + FC-170C combined prior to preparation	1.29	0.05	0.08	0.09	0.09
I6-2: GAA + TPOZ combined prior to preparation	1.25	0.07	0.11	0.14	0.14
I7-2: GTMS + TPOZ combined prior to preparation	1.24	0.07	0.18	0.19	0.19
I8-2: GTMS + TPOZ + FC-170C combined prior to preparation	1.28	0.01	0.17	0.18	0.18

Table 5.2-7: Wedge Test Results for Sol-Gel Panels Prepared without FC-170C Surfactant; 7-Week-Old Kits with Premixed Components

Sample Condition	Initial (in)	Cumulative Crack Growth (in)			
		24hr	168hr	336hr	504hr
S2-2: TPOZ + IPA combined prior to preparation	1.27	0.03	0.15	0.17	0.17
S3-2: GTMS + TPOZ combined prior to preparation	1.27	0.06	0.13	0.15	0.15
RS1: Control, no pre-mixing of components	1.22	0.10	0.12	0.12	0.12

Table 5.2-8: Wedge Test Results for Sol-Gel Panels Prepared without FC-170C Surfactant or IPA; 7-Week-Old Kits with Premixed Components

Sample Condition	Initial (in)	Cumulative Crack Growth (in)			
		24hr	168hr	336hr	504hr
SI2-2: GAA + TPOZ combined prior to preparation	1.28	0.09	0.17	0.18	0.18
RSI1: Control, no pre-mixing of components	1.21	0.12	0.16	0.16	0.16

The premixed solutions of GAA and TPOZ form a solid, white mass that is difficult to remove from the bottle to prepare the sol-gel solution. Ideally for ease of use, all kit components should remain in solution. It was determined that adding a small amount of deionized water to the solution of GAA and TPOZ stabilizes the liquid phase. Ongoing FTIR analysis, Figure 5.2-1, has shown this solution to be stable over time.

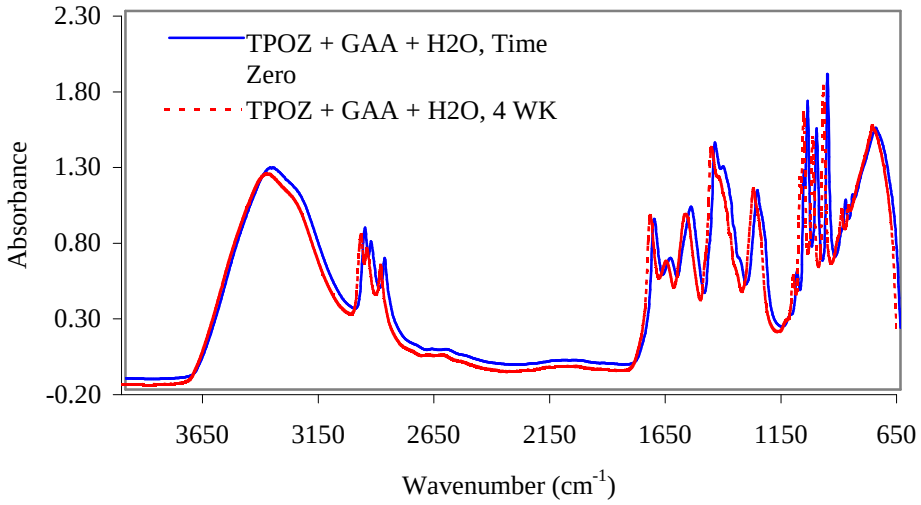


Figure 5.2-1: FTIR Spectra of TPOZ/GAA/H_2O Solutions Showing Changes in Stability Between the Initial Mixing and 4 Weeks. Overlapping Peaks Show That the Mixture is Essentially Stable Over This Time Period

5.2.3 Six-Month Old Kits

The wedge test data for kits aged for six months are shown in Table 5.2-9, Table 5.2-10, Table 5.2-11, and Table 5.2-12.

Table 5.2-9: Wedge Test Results for Specimens with All Components (6-Month Shelf Life)

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24h	168hr	336hr	504hr	
A2-3: GAA + TPOZ + IPA combined prior to preparation	1.21	0.13	0.20	0.20	0.20	97% co
A3-3: GTMS + TPOZ + IPA combined prior to preparation	1.16	0.15	0.21	0.21	0.21	72% co
RA1: Control, no pre-mixing of components	1.24	0.08	0.08	0.09	0.09	

* co: cohesive failure within the adhesive layer

Table 5.2-10: Total Crack Length for Original Kitting Trial 3 Specimens Without IPA (6-Month Shelf Life)

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
RI1: Control, no pre-mixing of components	1.26	0.10	0.15	0.15	0.15	
I2-3: H20 + FC-170C combined prior to preparation	1.15	0.14	0.16	0.16	0.18	92% co
I3-3: GTMS + FC-170C combined prior to preparation	1.16	0.14	0.20	0.21	0.25	95% co
I6-3: GAA + TPOZ combined prior to preparation	1.15	0.11	0.17	0.18	0.21	98% co
I7-3: GTMS + TPOZ combined prior to preparation	1.12	0.16	0.22	0.26	0.26	86% co
I8-3: GTMS + TPOZ + FC-170C combined prior to preparation	1.15	0.15	0.22	0.25	0.25	96% co

* co: cohesive failure within the adhesive layer

Table 5.2-11: Wedge Test Results for Specimens Without Surfactant (6-Month Shelf Life)

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
S2-3: TPOZ + IPA combined prior to preparation	1.15	0.09	0.14	0.17	0.19	94% co
S3-3: GTMS + TPOZ combined prior to preparation	1.17	0.13	0.19	0.21	0.23	75% co
RS1: Control, no pre-mixing of components	1.22	0.10	0.12	0.12	0.12	

* co: cohesive failure within the adhesive layer

Table 5.2-12: Wedge Test Results for Kitting Trial 3 Specimens Without IPA or Surfactant (6-Month Shelf Life)

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
SI2-3: GAA + TPOZ combined prior to preparation	1.13	0.13	0.22	0.27	0.27	95% co
RSI1: Control, no pre-mixing of components	1.21	0.12	0.16	0.16	0.16	

* co: cohesive failure within the adhesive layer

5.2.4 Twelve-Month Old Kits

The wedge test results for year-old kits containing all components are given in Table 5.2-13. The results for year-old kits without IPA are shown in Table 5.2-14. Table 5.2-15 illustrates the wedge test results for year-old kits without surfactant. Wedge test results for year-old kits without surfactant or IPA are in Table 5.2-16.

Table 5.2-13: Wedge Test Results for Year-Old First-Generation Kits with All Components

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
A2-4: GAA + TPOZ + IPA combined prior to preparation	1.21	0.07	0.14	0.22	0.22	97% co
A3-4: GTMS + TPOZ + IPA combined prior to preparation	1.21	0.10	0.18	0.27	0.28	21% co
RA1: Control, no pre-mixing of components	1.24	0.08	0.08	0.09	0.09	

* co: cohesive failure within the adhesive layer

Table 5.2-14: Wedge Test Results Year-Old First-Generation Kits without IPA

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
RI1: Control, no pre-mixing of components	1.26	0.10	0.15	0.15	0.15	
I2-4: H20 + FC-170C combined prior to preparation	1.19	0.05	0.13	0.19	0.19	98% co
I3-4: GTMS + FC-170C combined prior to preparation	1.20	0.03	0.14	0.16	0.16	96% co
I6-4: GAA + TPOZ combined prior to preparation	1.25	0.06	0.12	0.16	0.16	97% co
I7-4: GTMS + TPOZ combined prior to preparation	1.27	0.16	0.19	0.25	0.25	95% co
I8-4: GTMS + TPOZ + FC-170C combined prior to preparation	1.23	0.13	0.21	0.24	0.24	79% co

* co: cohesive failure within the adhesive layer

Table 5.2-15: Wedge Test Results Year-Old First-Generation Kits Without Surfactant

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
S3-4: GTMS + TPOZ combined prior to preparation	1.19	0.10	0.19	0.26	0.26	30% co
RS1: Control, no pre-mixing of components	1.22	0.10	0.12	0.12	0.12	

* co: cohesive failure within the adhesive layer

Table 5.2-16: Wedge Test Results for Year-Old First-Generation Kits Without Surfactant or IPA

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
SI2-4: GAA + TPOZ combined prior to preparation	1.18	0.08	0.16	0.21	0.24	97% co
RSI1: Control, no pre-mixing of components	1.21	0.12	0.16	0.16	0.16	

* co: cohesive failure within the adhesive layer

These results indicate that some sol-gel kit configurations, when packaged in appropriate packaging materials, can survive a minimum twelve-month shelf life. In general, precombining the silane component in any manner appeared to degrade the performance of the premixed component kit configuration. Additions of isopropyl alcohol did not significantly affect or improve the performance of the kits. Precombining the glacial acetic acid and zirconium components will most likely provide a stable configuration for storing. These results will be validated in follow-on kitting studies.

5.3 Sprayer Equipment

A test was executed according to the matrix in Table 5.3-1 to study the potential for sprayers to be included in a kit. Ease of use as well as the effect of these sprayers on the adhesion of the applied sol-gel coating was evaluated. Six 2024-T3 panels (6 inch x 6 inch) were sprayed with sol-gel solution using three different sprayers: 1) an HVLP gun, 2) a Preval Power Unit, 2.1oz can (Precision Valve Corporation), and 3) an RL Flo-Master Home & Garden Sprayer, model no. 1998 (Root Lowell Manufacturing Company). The Preval sprayer consists of a polypropylene receptacle for holding the solution that is screwed onto a pressurized container filled with a propellant. A siphon tube leads to the bottom of the holding vessel to draw up solution through a spray nozzle. The RL Flo-Master sprayer consists of a polypropylene vessel for holding the solution, which is connected to a top sprayer. The container is pressurized using a manually applied pumping action, similar to commonly used garden sprayers.

Table 5.3-1: Sprayer Test Matrix

Specimen ID	Surface Pretreatment	Sprayer Type
A-67-H1	#180 Alumina Grit-blast	HVLP
A-67-H2	#180 Alumina Grit-blast	HVLP
A-67-P1	#180 Alumina Grit-blast	Preval
A-67-P2	#180 Alumina Grit-blast	Preval
A-67-F1	#180 Alumina Grit-blast	RL Flo-Master
A-67-F2	#180 Alumina Grit-blast	RL Flo-Master

The following observations were made regarding the Preval and RL Flo-Master sprayers:

- The Preval sprayer was set to "SPRAY", but toward "STREAM" to narrow the region of spray and control application.
- The Preval and Flo-Master sprayers used 3-4 times as much sol-gel solution as the HVLP to coat 2 panels (approximately 500-600ml).
- Both the Preval and Flo-Master sprayers must have 300-400ml of solution in the container to spray properly, due to the length of the uptake tube. This is not true of the HVLP gun.
- The ergonomics of the Preval sprayer were less than optimum due to the need to constantly pump the trigger. Pumping of the trigger also resulted in a splatter-like application. It did not yield a steady stream of solution as did the HVLP spray gun.
- It was necessary to re-pressurize the Flo-Master twice during the 3-minute application period. This procedure involved pumping the handle 10-20 times.
- The Flo-Master is similar to the HVLP spray gun in that the button is held down during the entire application period, so a more constant flow of sol-gel solution is achieved.

All wedge test panels in these matrices were grit-blasted, spray coated with Boegel-EPII, and primed with Cytec BR 6747-1 (precure), and bonded with AF 163-2M adhesive. Table 5.3-2 shows the total crack length for the three different sprayers tested: H = HVLP Gun, P = Preval Sprayer, and F = RL Flo-Master Garden Sprayer. The use of the Flo-Master led to slightly smaller crack lengths than did the HVLP gun control. The average crack length for the Flo-Master specimens leveled out after 168 hours of exposure. The crack growths for each sprayer type were less than 0.25 inches over one month of hot/wet exposure. Both the Preval and the Flo-Master sprayer yielded specimens with smaller crack growths than those resulting from the use of the HVLP spray gun. This test demonstrated that sol-gel coating performance similar to those obtained using the HVLP spray gun could be achieved using inexpensive, disposable sprayers.

Table 5.3-2: Wedge Test Results for Various Sprayers: H = HVLP gun, P = Preval Sprayer, F = RL Flo-Master Garden Sprayer

Sample Condition	Initial (in)	Cumulative Crack Growth (hrs)				Failure Mode*
		24	168	336	504	
A-67-H	1.20	0.02	0.13	0.13	0.14	97% co
A-67-P	1.23	0.01	0.12	0.12	0.16	95% co
A-67-F	1.20	0.01	0.10	0.10	0.10	93% co

* co: cohesive failure within the adhesive layer

5.4 Kit Formulation Tolerance Measurements

Sol-gel specimens were prepared according to the test matrix in Table 5.4-1 in order to determine the tolerances in the sol-gel formulation. This would simulate conditions in which the kits were not properly constructed or the formulation was not properly measured out. The wedge test adherends were grit-blasted followed by sol-gel application via HVLP spray gun, as specified. After the typical 3-minute wet time, adherends were dried at approximately 70°F for 30-60 minutes, primed with Cytec BR 6747-1 (precured), and autoclave bonded with 3M AF163-2M adhesive. Adding or subtracting 10% from one or more components was tested to ascertain the tolerance level of chemicals in the sol-gel formulation. Wedge crack extension performance is reported in Table 5.4-2.

Table 5.4-1: Tolerance Matrix Specimens

Specimen*	Formulation
T-C	Boegel-EPII
T-A3	Boegel-EPII + 10% more GAA, GTMS, TPOZ
T-AS	Boegel-EPII + 10% more GTMS
T-AZ	Boegel-EPII + 10% more TPOZ
T-S3	Boegel-EPII less 10% GAA, GTMS, TPOZ
T-SS	Boegel-EPII less 10% GTMS
T-SA	Boegel-EPII less 10% GAA
T-SZ	Boegel-EPII less 10% TPOZ

* 10 specimens (two panels) for each case

Table 5.4-2: Wedge Test Results for Tolerance Matrix

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
T-A3	1.188	1.23	1.33	1.33	1.34	97
T-AS	1.206	1.27	1.34	1.34	1.38	96
T-AZ	1.222	1.33	1.39	1.39	1.40	93
T-S3	1.158	1.20	1.34	1.34	1.35	77
T-SS	1.244	1.28	1.39	1.41	1.42	98
T-SA	1.234	1.28	1.33	1.34	1.36	97
T-SZ	1.194	1.22	1.34	1.35	1.36	66

* co: cohesive failure within the adhesive layer

The failure modes for most of the specimens were similar, with one striking exception. Specimens prepared with 10% less TPOZ and 10% less of TPOZ, GAA, and GTMS yield significantly worse failure modes. Since the failure modes for 10% less GAA and 10% less GTMS were >97% cohesive, it is probable that the variation in TPOZ is the critical factor.

Table 5.4-2 illustrates the wedge test data of the tolerance matrix specimens over 500 hours of exposure to 140°F and 98% relative humidity. With the exception of specimens with 10% more TPOZ and 10% less GTMS, all specimens were approximately equal in performance to the control. All specimens showed relatively similar crack growth with less than 0.25 inch of crack

growth over 30 days in a hot/wet environment. The specimen with 10% less GAA showed less crack growth than the control.

The sol-gel solution is fairly forgiving of variations up to 10% in component amounts, with the exception of reduced TPOZ. Since it is unlikely that such a large variation would become evident in a kit manufacturing facility, such tolerances are conducive to inexpensive kit production.

5.5 Second-Generation Kit Studies

In order to make sol-gel technology viable for use on DoD weapon systems, a process for creating and storing a quality sol-gel product was optimized. The first portion of this effort focused on identifying which components could be stored together for an extended period of time and still result in acceptable bonding performance. Several kitting options proved that the sol-gel materials could be stored for up to a year.

The second-generation kitting experiments were initiated to investigate the improvements in kitting procedures that have been learned since initiating the original kitting experiments. The difference is that the second-generation kits (1) use improved packaging materials to prevent solution leakage and oxygen or moisture permeation and (2) use improved premixing techniques and combinations of chemicals that should yield increased stability over time.

5.5.1 Unaged Second-generation Kits

The constituents of the second-generation 2- and 3-part kits are given in Table 5.5-1. The wedge test data for the second-generation 2- and 3-part kits with no shelf-life aging are shown in Table 5.5-2. The average failure modes were: Kit 1 - 96% cohesive, Kit 2 - 92% cohesive, and Kit 3 - 95% cohesive. Sol-gel was applied over #180 alumina grit-blasted Al 2024-T3. Adherends were primed with BR 6747-1 (precured) and bonded with AF 163-2M. Conditioning was conducted at 140°F and >95% RH.

Table 5.5-1: Second-Generation 2-Part and 3-Part Sol-Gel Kit Components

Kit Number	Container 1	Container 2	Container 3	Container 4	Container 5
1	H_2O, surfactant, GAA, and TPOZ	GTMS			
2	H_2O and surfactant	GTMS	GAA, TPOZ, H_2O		
3	H_2O and surfactant	GTMS	GAA, TPOZ, IPA		
Control	H_2O and surfactant	GTMS	Empty	GAA	TPOZ

Table 5.5-2: Wedge Test Results for Unaged Second-Generation 2-Part and 3-Part Kits

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
A-106-1-0: 2-part	1.19	0.10	0.21	0.21	0.21	96% co
A-106-2-0: 3-part w/water	1.22	0.08	0.13	0.13	0.16	92% co
A-107-3-0: 3-part w/IPA	1.18	0.06	0.15	0.15	0.15	95% co
A-119-C-0: 5-part	1.18	0.11	0.14	0.17	0.18	96% co

* co: cohesive failure within the adhesive layer

5.5.2 One-Month Old Second-Generation Kits

The wedge test data for the 2- and 3-part kits aged for one month are given in Table 5.5-3.

Table 5.5-3: Wedge Test Results for Second-Generation 2-Part and 3-Part Kits (1-Month Shelf Life)

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
A-107-1-1: 2-part	1.21	0.13	0.17	0.21	0.21	96% co
A-109-2-1: 3-part w/water	1.20	0.08	0.14	0.18	0.18	96% co
A-109-3-1: 3-part w/IPA	1.23	0.14	0.16	0.16	0.18	95% co
A-114-C-1: 5- part	1.17	0.04	0.16	0.18	0.19	96% co

* co: cohesive failure within the adhesive layer

5.5.3 Six-Month Old Second-Generation Kits

Specimens were prepared from 6-month old kits, according to Table 5.5-4. Six-month shelf life wedge test data for the kitted options are shown in Table 5.5-5. These are compared against the control, which has all of the components packaged separately.

Table 5.5-4: Six-Month Old Second-Generation Kit Matrix

Kit Number	Container 1	Container 2	Container 3	Container 4	Container 5
1	H_2O, surfactant, GAA, and TPOZ	GTMS			
2	H_2O and surfactant	GTMS	GAA, TPOZ, H_2O		
3	H_2O and surfactant	GTMS	GAA, TPOZ, IPA		
Control	H_2O and surfactant	GTMS	Empty	GAA	TPOZ

Table 5.5-5: Wedge Test Results for Second-Generation 2-Part and 3-Part Kits (6-Month Shelf Life)

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
A-110-1-6: 2-part	1.20	0.10	0.16	0.16	0.16	96% co
A-110-2-6: 3-part w/water	1.24	0.11	0.13	0.13	0.13	92% co
A-110-3-6: 3-part w/IPA	1.18	0.13	0.18	0.20	0.20	95% co
A-114-C-6: 5-part	1.16	0.12	0.16	0.18	0.18	95% co

* co: cohesive failure within the adhesive layer

5.5.4 Twelve-Month Old Second-Generation Kits

Bonded panels were prepared from one-year old second-generation kits. Sol-gel solutions prepared from each kit were coated over #180 alumina grit-blasted, Scotch-Brite™ abraded, and alumina paper (3M 326U #220) abraded Al 2024-T3 bare wedge test adherends as well as Scotch-Brite™ abraded peel test substrates. The wedge test results are given in Table 5.5-6 and Table 5.5-7. All grit-blasted specimens exhibited 97-100% cohesive failures after 24 hours of exposure. All alumina-abraded specimens had 95-97% cohesive failures after 24 hours of exposure. Sol-gel solution from the 2-part kit when applied over Scotch-Brite™ abraded panels resulted in 75% cohesive failures after 24 hours of exposure. Control kit sol-gel applied over Scotch-Brite™ abraded panels gave 85% cohesive failures after 24 hours of exposure. Sol-gel solution from 3-part kits applied over Scotch-Brite™ abraded panels showed 90% cohesive failure after 24 hours of exposure. The failure modes after six weeks of exposure are given in Table 5.5-8. Failure modes for the Scotch-Brite™ abraded panels were unusually poor. The abraded panels were added to the shelf-life matrix because abrasion pretreatment are believed to be more sensitive to process changes than are grit-blasted surfaces. It is possible use of the older sol-gel kits is resulting in reduced wedge test performance. However, it is more likely the Scotch-Brite™ abraded panels are not optimal for some other unknown reason(s) since the control kit failure mode is only 22% cohesive. The optimized nylon-pad/sol-gel process yields over 90% cohesive failures in the 120°F wedge test (Table 2.3-3).

Table 5.5-6: Wedge Test Results for Second-Generation 2-Part and 3-Part Kits (12-Month Shelf Life)

Sample Condition	Initial (in)	Cumulative Crack Growth (in)				Failure Mode*
		24hr	168hr	336hr	504hr	
A-111-1-12A: 2-part	1.22	0.10	0.17	0.17	0.24	98% co
A-111-2-12A: 3-part w/water	1.22	0.11	0.15	0.15	0.16	97% co
A-111-3-12A: 3-part w/IPA	1.19	0.11	0.17	0.17	0.18	97% co
A-115-C-12A: 5-part	1.25	0.10	0.16	0.16	0.16	96% co

* co: cohesive failure within the adhesive layer

Table 5.5-7: Wedge Test Data for All Specimens Prepared from One-Year Old Second-Generation Kits

Sample Condition	Initial (in)	Cumulative Crack Growth (in)			
		24hr	168hr	336hr	504hr
A-111-1-12A: Boegel-EPII from a year old 2-part kit over grit-blasted 2024-T3	1.22	0.10	0.17	0.17	0.24
A-111-1-12B: Boegel-EPII from a year old 2-part kit over Scotch-Brite™ abraded 2024-T3	1.21	0.21	0.35	0.46	0.46
A-111-1-12C: Boegel-EPII from a year old 2-part kit over sanded 2024-T3	1.22	0.14	0.23	0.28	0.28
A-111-2-12A: Boegel-EPII from a year old 3-part w/water kit over grit-blasted 2024-T3	1.22	0.11	0.15	0.15	0.16
A-111-2-12B: Boegel-EPII from a year old 3-part w/water kit over Scotch-Brite™ abraded 2024-T3	1.19	0.18	0.18	0.36	0.36
A-111-2-12C: Boegel-EPII from a year old 3-part w/water kit over sanded 2024-T3	1.18	0.17	0.22	0.34	0.35
A-111-3-12A: Boegel-EPII from a year old 3-part w/IPA kit over grit-blasted 2024-T3	1.19	0.11	0.17	0.17	0.18
A-111-3-12B: Boegel-EPII from a year old 3-part w/IPA kit over Scotch-Brite™ abraded 2024-T3	1.09	0.25	0.42	0.51	0.51
A-111-3-12C: Boegel-EPII from a year old 3-part w/IPA kit over sanded 2024-T3	1.13	0.21	0.31	0.43	0.43
A-115-C-12A: Boegel-EPII from a year old 5-part kit over grit-blasted 2024-T3	1.25	0.10	0.16	0.16	0.16
A-115-C-12B: Boegel-EPII from a year old 5-part kit over Scotch-Brite™ abraded 2024-T3	1.21	0.18	0.28	0.34	0.36
A-115-C-12C: Boegel-EPII from a year old 5-part kit over sanded 2024-T3	1.19	0.14	0.19	0.28	0.28

* co: cohesive failure within the adhesive layer

Table 5.5-8: Failure Modes of Specimens Prepared from 1-Year Old Kits After Six Weeks of Exposure (Wedge Test)

Kit	Alumina Abraded Substrate	Scotch-Brite™ Abraded Substrate	Grit-blasted Substrate
Control Kit	67% cohesive	22% cohesive	90% cohesive
2-Part Kit	82% cohesive	20% cohesive	97% cohesive
3-Part with Water	58% cohesive	47% cohesive	98% cohesive
3-Part with IPA	25% cohesive	23% cohesive	98% cohesive

A comparison of wedge test performance for grit-blasted specimens prepared from second-generation kits is shown in Figure 5.5-1. All failure modes are 95% cohesive unless otherwise noted. The bars show crack extension and the lines show the total crack length.

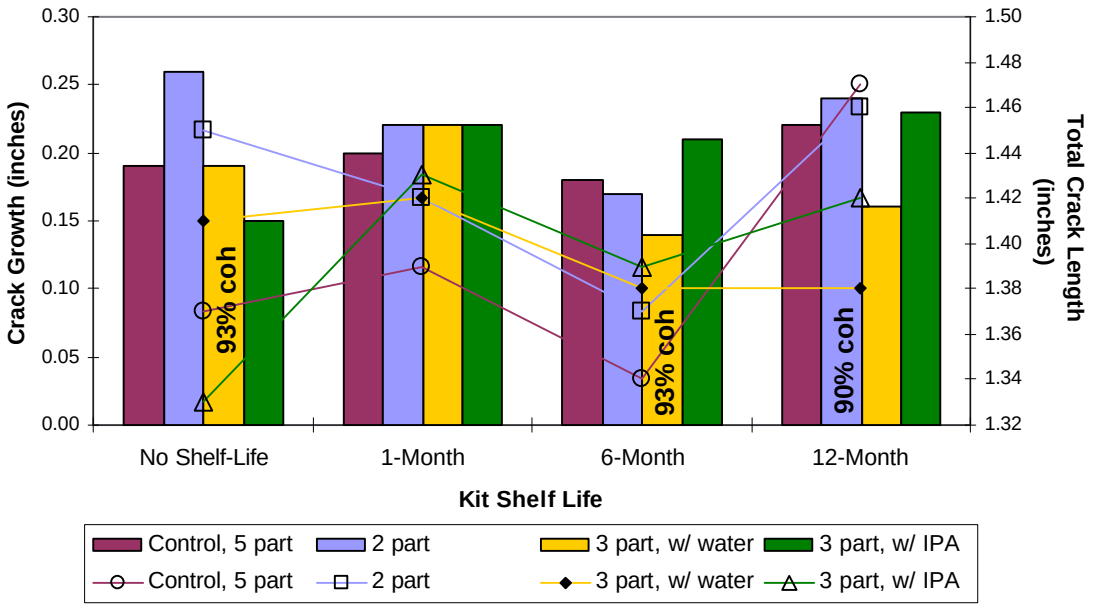


Figure 5.5-1: Comparison of Grit-Blasted Specimens Prepared from Kits of Different Ages After 1000 Hours of Exposure to 140°F and 98% RH

5.6 Simplified Kit Mixing

A kit mixing procedure that greatly simplifies the stepwise sequence of chemical mixing was tested for its end-effects on bond durability. The original kit mixing procedure is shown in Table 5.6-1. To test variations of this mix process, wedge test substrates of Al 2024-T3 bare were grit-blasted and coated with Boegel-EPII mixed according to the variables in Table 5.6-2. All were primed with Cytec BR 6747-1 within 24 hours and were bonded with AF 163-2M. Wedge test results are given in Table 5.6-3. All yielded approximately 98% cohesive failure modes after 1000 hours of exposure.

Table 5.6-1: Boegel-EPII Standard Mixing Instructions

Step	Chemicals	Procedure
1	Zirconium n-Propoxide (TPOZ) Glacial Acetic Acid (GAA)	Mix TPOZ & GAA in small vial. Agitate until fully mixed. Mixture should be warm since reaction is exothermic. Let sit for 10-15 minutes.
2	γ-glycidoxypropyltrimethoxysilane (GTMS) Deionized water	Mix GTMS and water in a flask using magnetic mixer.
3	GAA & TPOZ mixture GTMS & water mixture	After 10-15 minutes has elapsed, pour GAA/TPOZ mixture into GTMS/water mixture.
4	Boegel-EPII sol-gel solution	Mix with magnetic mixer for a minimum of 30 minutes. Boegel-EPII solution must be used within 10 hours of initial mixing.

Table 5.6-2: Simplification of Kit Mixing Test Matrix

Specimen ID	Variable
C134-1	None, Control
C134-2	Mix TPOZ/GAA for 30 seconds instead of 10 minutes
C134-3	Add TPOZ/GAA mixture simultaneously with GTMS
C134-4	Add TPOZ/GAA/Water mixture simultaneously with GTMS
C134-5	Add TPOZ/GAA/IPA mixture simultaneously with GTMS

Table 5.6-3: Wedge Test Results for Specimens Made Using the Simplified Mix Process and Sol-Gel Kits

Surface Preparation*	Initial (in)	Cumulative Crack Growth (in)			
		24hr	168hr	336hr	504hr
C134-1	1.22	1.33	1.34	1.36	1.36
C134-2	1.23	1.32	1.36	1.38	1.38
C134-3	1.22	1.31	1.34	1.34	1.34
C134-4	1.18	1.31	1.32	1.32	1.32
C134-5	1.21	1.34	1.36	1.37	1.38

* Reference Table 5.6-2

Standard mixing instructions require the mixture to sit for 10-15 minutes upon mixing the TPOZ and GAA (step #3). In order to simplify the transition and enhance the robustness of the process, the sol-gel mixing procedures were simplified. Additional testing was conducted to verify the equivalency of the simplified mix for the sol-gel surface preparation. Using FTIR, it was determined that reducing the mix times in combining the separate components of the formulation resulted in no chemical difference in the formulation. A mixing process was developed in which the TPOZ and GAA mixture only required 1-3 minutes to stabilize prior to stirring with the water/silane mixture. Wait times between the process steps were eliminated, and the wording of the procedures was simplified for clearer understanding, regardless of level of familiarity with sol-gel coating technology. The revised procedure is presented in Table 5.6-4. For kits associated with this procedure, Syringe A1 contains the premeasured GTMS, Container A holds the appropriate amount of water, while Syringes B1 and B2 contain the premeasured GAA and TPOZ.

Table 5.6-4: Sol-Gel Simplified Kit Mix Procedure

The sol-gel solution, Boegel-EPII, shall be prepared according to the kitting procedure shown. Use kit size appropriate for size of area to be treated. For example, approximately 100ml of the sol-gel solution will be enough to coat about 2 square feet of surface area. Scale up as required.			
Step	**Procedure**	**Equipment**	**Control**
1	Dispense Syringe A1 into Container A and shake or agitate for 1-3 minutes.	Syringe A1 Container A	Liquid in Syringe A1 and Container A should be clear and colorless. Mixture should be clear and colorless.
2	Dispense Syringe B1 into empty Container B. CAUTION: Avoid skin contact with the liquid.	Syringe B1 Container B	Liquid in Syringe B1 should be clear and colorless. Container B should be clean and empty prior to use.
3	Dispense Syringe B2 into Container B and shake or agitate for 1-3 minutes. CAUTION: Some heat may be released as the reaction is exothermic.	Syringe B2 Container B	Syringe B2: There should be no white particles in the yellow liquid. White matter clogging the syringe tip is acceptable. If syringe is clogged, pull back slightly on the plunger to release the clog and dispense liquid.
4	Pour Container B contents into Container A. Shake vigorously for 1-3 minutes.	Container A Container B	Solution should be clear to slightly cloudy (milky).
5	Allow solution in Container A to sit at room temperature for a minimum induction time of 30 minutes.	Container A	
6	Shake Container A for a minimum of one minute immediately prior to application.	Container A	
The induction time for the sol-gel solution is 30 minutes. The pot-life of the mixed solution is 10 hours after induction time is complete. Clearly label the sol-gel solution with the allowed application period or pot-life (time from completion of step 5 plus 10 hours).			

5.6.1 Verification of Simplified Mix Process for Kits

The simplified mix process was verified at Boeing by performing tests on grit-blasted, sanded and Scotch-Brite™ abraded bare 2024-T3 aluminum alloy. Two sets of each were treated with Boegel-EPII, primed with Cytec BR6747-1, and bonded using AF 163-2M adhesive. Parallel sets were prepared using the standard lab-mixed procedure. The wedge test results are presented in Table 5.6-5and Table 5.6-6. No significant differences were seen between the standard mix and simplified mix procedures.

Table 5.6-5: Wedge Test Results for Standard Sol-Gel Mix Procedures

Mix Procedure/Conditions	**Initial (in)**	**Cumulative Crack Growth (in)**				
		24hr	**120hr**	**384hr**	**576hr**	**720hr**
AA04-1 Std Mix/GB	1.25	0.05	0.11	0.14	0.14	0.14
AA04-2 Std Mix/GB	1.22	0.06	0.10	0.10	0.10	0.10
AA04-3- Std Mix/Sand	1.25	0.12	0.15	0.15	0.16	0.17
AA04-4 Std Mix/Sand	1.27	0.13	0.19	0.19	0.19	0.20
AA04-5 Std Mix/SB	1.22	0.11	0.21	0.21	0.26	0.27
AA04-6 Std Mix/SB	1.24	0.12	0.16	0.16	0.16	0.16

GB: grit-blast; Sand: alumina paper; SB: Scotch-Brite™

Table 5.6-6: Wedge Test Results for Simplified Sol-Gel Mix Procedures

Mix Procedure/Conditions	Initial (in)	Cumulative Crack Growth (in)					
		24hr	168hr	336hr	504hr	672hr	1008hr
AA04-1x Simplified Mix/GB	1.29	0.14	0.18	0.18	0.18	0.21	0.21
AA04-2x Simplified Mix/GB	1.22	0.14	0.16	0.16	0.16	0.16	0.16
AA04-3x Simplified Mix/Sand	1.26	0.15	0.21	0.21	0.21	0.23	0.23
AA04-4x Simplified Mix/Sand	1.25	0.16	0.18	0.18	0.20	0.20	0.22
AA04-5x Simplified Mix/SB	1.23	0.16	0.26	0.26	0.29	0.32	0.32
AA04-6x Simplified Mix/SB	1.26	0.14	0.23	0.23	0.23	0.23	0.23

GB: grit-blast; Sand: alumina paper; SB: Scotch-Brite™

5.6.2 Verification Testing for the Effect of Simplified Boegel-EPII Mixing Process

Wedge tests were performed on Al 2024-T3 adherends using both the standard and simplified mixing processes over three different deoxidation steps. Wedge tests were conducted at 140°F and 95-100% RH. Results are shown in Table 5.6-7. After the Boegel-EPII application, adherends were primed with BR 6747-1 and bonded with AF 163-2M. Primer was both precured and cocured for the case of adherends pretreated by nylon-pad abrasion and was precured for the others. The wedge test specimens processed using the simplified mixing procedure performed as well as panels processed with the standard mixing procedure using all deoxidation processes.

Table 5.6-7: Standard Boegel-EPII Mixing versus Simplified Mixing

Deoxidation Step	Mixing	Initial (in)	Cumulative Crack Growth (in)							Failure Mode*
			1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
Grit-blast	Standard	1.12	0.05	0.06	0.11	0.18	0.22	0.25	0.26	96% co
	Simplified	1.09	0.04	0.10	0.14	0.22	0.28	0.29	0.33	94% co
3M 326U #220 "Sandpaper"	Standard	1.18	0.06	0.13	0.27	0.50	0.68	0.74	0.78	17% co
	Simplified	1.09	0.05	0.11	0.15	0.24	0.37	0.47	0.57	25% co
Nylon pad (precure)	Standard	1.13	0.06	0.10	0.13	0.19	0.25	0.29	0.33	68% co
	Simplified	1.19	0.04	0.10	0.14	0.22	0.28	0.34	0.35	81% co
Nylon pad (cocure)	Standard	1.09	0.05	0.11	0.15	0.22	0.26	0.29	0.33	86% co
	Simplified	1.10	0.04	0.09	0.13	0.20	0.28	0.28	0.31	89% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

5.7 Vendor-Supplied Sol-Gel Kit Evaluation

Tests of prototype sol-gel kits prepared by an external vendor were conducted to confirm the performance on aluminum alloy. A prototype dual-pack GAA/TPOZ was received from a commercial vendor (no longer supplying kits; not AC Tech). Upon receipt, the outside of the package had an acetic acid odor, suggesting the dual-pack polymeric packaging material is somewhat permeable to GAA or that a small amount was spilled onto the outside the pack during preparation leaving residual material.

Initial testing of the prototype kit showed that it was relatively inconvenient to use. It was noted that there was some white precipitate in the TPOZ side of the bag before it was opened. The

white precipitate remained in the mixture of TPOZ and GAA even after mixing. However, the experiment was allowed to proceed with these inferior materials. It was difficult to remove all of the material from the package. The technician rolled the plastic bag down from the top to the bottom to try and get all of the material out of the bag, but it was a messy and inexact process. The bag and material were weighed before and after to make sure that an appropriate amount of material was deployed from the package. The weight of the material removed from the package was 7.19 grams of the 7.25 grams that theoretically should have been in the package, a loss of about 1% of the weight.

The mixing process was accomplished by removing the clip at the middle of the clip-pack and manipulating the package. The mixing was continued for ten minutes to keep with the standard mixing procedure. At the conclusion of the mix period, the TPOZ/GAA mixture was dispensed by cutting off a corner of the package and pouring the contents into the mix vessel through the cut opening. It is important to note that a scissors was required to open the package. Use of extraneous tools is undesirable since they may or may not be available at the repair location site.

Two sets of #180 grit-blasted (1212-1 & 4) and two sets of 3M 326U #220 alumina-abraded (1212-6 & 8) Al 2024-T3 6-inch x 6-inch wedge test adherends were treated with Boegel-EPII from the prototype kit, primed with Cytec BR6747-1, and bonded with 3M AF163-2M. Specimens pulled evaluated after 2 weeks yielded failure modes of 99% cohesive and 94% cohesive for grit-blasted and sanded specimens, respectively. Wedge test results are presented in Table 5.7-1. Although the results are good, additional development of simple kits will be carried out in conjunction with commercial sol-gel kit suppliers since the kit was not convenient to use.

Table 5.7-1: Prototype Vendor-Supplied Kit Performance (Standard Mix Procedure)

Pretreatment	**Initial (in)**	**Cumulative Crack Growth (in)**						**Failure Mode***
		24hr	**168hr**	**336hr**	**504hr**	**672hr**	**1008hr**	
AA07-1A; Grit-blast	1.22	0.06	0.13	0.13	0.13	0.13	0.13	99% co
AA07-1B; Grit-blast	1.19	0.07	0.10	0.10	0.10	0.10	0.10	99% co
AA07-2A; #220 alumina abrade	1.22	0.08	0.15	0.15	0.15	0.15	0.15	94% co
AA07-2B; #220 alumina abrade	1.19	0.11	0.19	0.19	0.19	0.19	0.19	94% co

* co: cohesive failure within the adhesive layer

5.8 Evaluation of Boegel-EPII Sol-Gel Solution Parameters

Several additional experiments were conducted to determine the significance of parameters such as GTMS manufacturer, simplified mixing procedures, constant mixing versus occasional shaking, and the maximum pot-life of Boegel-EPII.

5.8.1 Effect of GTMS Manufacturer

Gelest, Inc. and Dow Corning, Inc. are two of several companies that manufacture γ-glycidoxypropyltrimethoxysilane (GTMS). Batches of Boegel-EPII solution were prepared using standard mixing procedures (Table 5.6-1) with Dow Corning Z-6040 and Gelest SIG5840.0. Wedge test panels were fabricated using both grit-blast and nylon-pad surface activation methods and Boegel-EPII mixed with GTMS from the two manufacturers. A total of four wedge test panels were fabricated with Al 2024-T3, representing one panel for each

condition above. Specimens were tested at 140°F and 95-100% RH. Results are shown in Table 5.8-1. There did not appear to be any difference in wedge test results due to the GTMS source. The crack growth and failure modes of specimens deoxidized in the same manner appeared to be equivalent.

Table 5.8-1: Effect of GTMS Manufacturer on Wedge Test Results

Deox Step	GTMS Source	Initial (in)	Cumulative Crack Growth (in)							Failure Mode*
			1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
Grit-blast	Dow Corning	1.14	0.03	0.07	0.10	0.19	0.25	0.27	0.29	99% co
	Gelest	1.16	0.02	0.03	0.05	0.17	0.22	0.24	0.25	98% co
3M Roloc Medium	Dow Corning	1.12	0.02	0.07	0.10	0.22	0.26	0.28	0.30	88% co
	Gelest	1.07	0.00	0.01	0.06	0.20	0.26	0.26	0.29	86% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

5.8.2 Effect of GTMS Concentration

A set of Al 2024-T3 wedge test samples was prepared to evaluate the effect of increases in the concentration of the Boegel-EPII solution. In prior work, different concentrations of sol-gel were evaluated, but a concentration evaluation was repeated, since many process and formulation changes had occurred since the original evaluation. Also, the addition of 5% (by volume) of GTMS to the Cytec BR 6747-1 primer was evaluated as a way to populate the primer interfaces with extra active functional groups. Each panel was abraded for 3 minutes with one piece of #220 alumina paper. The 30% BR 6747-1 was diluted to 20% solids and used on these samples. Other preparation details for these samples are listed in the Table 5.8-2.

Table 5.8-2: S31 Concentration/Added Silane Sample Series Processing Details

Sample Number	Sol-Gel*	Application Method	Application Time	Drying Method	Drying Time	Primer	Adhesive
S 31-1	Boegel-EPII	Brush	2 Minutes	Air	110 Minutes	BR 6747-1	AF 163-2M
S 31-2	Boegel-EPII	Brush	2 Minutes	Air	104 Minutes	BR 6747-1 + 5 Vol. % GTMS	AF 163-2M
S 31-3	5X Boegel-EPII	Brush	2 Minutes	Air	77 Minutes	BR 6747-1	AF 163-2M
S 31-4	5X Boegel-EPII	Brush	2 Minutes	Air	73 Minutes	BR 6747-1 + 5 Vol. % GTMS	AF 163-2M

* 5X Boegel-EPII has 5 times the concentration of GTMS, TPOZ, and GAA

The performance of these samples is shown in Table 5.8-3. Sample S31-4, which was coated with the 15% Boegel-EPII solution and BR 6747-1 primer containing 5 volume percent GTMS, gave similar performance to the other #180 alumina grit-blasted 2024-T3 aluminum samples coated with the baseline sol-gel formulation and primer. As a result of these studies, no major change to the sol-gel formulation was made.

Table 5.8-3: Effect of GTMS Concentration on Sandpaper/Sol-Gel Wedge Crack Test Results

Mix Procedure/Conditions	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24 hr	168 hr	336 hr	504 hr	672 hr	1008 hr	
S 31-1: Boegel EP-II, No Surfactant, Standard BR 6747-1	1.20	0.13	0.19	0.19	0.19	0.19	0.22	87% co
S 31-2: Boegel EP-II, No Surfactant, BR 6747-1 + 5 Vol.% GTMS	1.24	0.13	0.19	0.19	0.19	0.21	0.22	81% co
S 31-3: 5X Boegel EP-II, No Surfactant, Standard BR 6747-1	1.26	0.12	0.18	0.18	0.18	0.18	0.21	89% co
S 31-4: 5X Boegel EP-II, No Surfactant, BR 6747-1 + 5 Vol.% GTMS	1.22	0.11	0.14	0.15	0.15	0.15	0.19	93% co

* co: cohesive failure within the adhesive layer

5.8.3 Effect of Constant Mixing Versus Occasional Mixing

Magnetic mixers such as those used to constantly mix Boegel-EPII solution in this program may not be available in all situations. Therefore an alternative mixing approach was evaluated. Two batches of sol-gel were prepared using standard sol-gel mixing instructions. One used constant mixing after all components were combined. A second batch was prepared by allowing the solution to sit for 30 minutes after combining the TPOZ/GAA mixture with the water/silane mixture. The solution was agitated intermittently by shaking the container during the 30-minute induction period. The container was also shaken immediately prior to use. Two Al 2024-T3 wedge test panels were fabricated per mix of Boegel-EPII solution, using nylon-pad deoxidation. Nylon-pad deoxidation was used because it tends to be more sensitive to process changes than grit-blasting. Specimens were tested at 120°F and 95-100% RH because nylon-pad/sol-gel performed correctly consistently yields good results when tested at these conditions. Results are shown in Table 5.8-4. There is little difference in the crack growth after 28 days between wedge test panels processed with different mixing methods for Boegel-EPII solution. The failure modes are also consistently around 92-93% cohesive with the remaining small amount of adhesional failure at the primer-metal interface.

Table 5.8-4: Occasional Shaking versus Constant Mixing of Boegel-EPII Solution

Mixing	Initial (in)	Cummulative Crack Growth (in)							Failure Mode*
		1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
Constant	1.00	0.06	0.07	0.07	0.11	0.12	0.13	0.17	92% co
	1.03	0.02	0.02	0.05	0.09	0.09	0.11	0.12	93% co
Occasional	1.03	0.06	0.06	0.07	0.12	0.12	0.15	0.16	92% co
	1.06	0.02	0.02	0.02	0.10	0.10	0.13	0.14	93% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

5.8.4 Pot-Life Evaluation

Previous data showed the Boegel-EPII remains active for a certain period of time after mixing. Relatively good bonding results were achieved when testing up to 24-hr old solutions. However, to ensure that the solution is good under all environmental processing conditions, a 10-hr pot-life after induction was recommended for the Boegel-EPII material. This would ensure that an entire work-shift could use a batch of material. In order to verify this time limit, a batch of Boegel-EPII was mixed according to the standard mixing procedures (Table 5.6-1). Once the TPOZ / GAA mixture was added to the GTMS / water mixture, a timer was set. Wedge test panels deoxidized with nylon pads were treated with sol-gel at various time intervals ranging from only 15 minutes to 72 hours in order to define an optimal operating window. One Al 2024-T3 wedge test panel (five specimens) per condition was fabricated using nylon-pad deoxidation. Panels were primed with BR 6747-1 cocured with AF 163-2M adhesive. Specimens were tested at 120°F and 95-100% RH. Results are shown in Table 5.8-5.

Although the standard mixing instructions require a minimum of 30 minutes for Boegel-EPII to mix prior to application, nylon-pad-abraded wedge test specimens treated after only 15 minutes of constant mixing exhibited cohesive failure modes. After 24 hours of mixing, the Boegel-EPII solution was very cloudy, although wedge test results still exhibited cohesive failures. After 48 hours of mixing, the Boegel-EPII solution was white and opaque, but wedge test results did not decrease substantially and still yielded 92% cohesive failure. After 72 hours of continuous mixing, the Boegel-EPII solution was opaque and contained small particulates. Wedge test results for panels coated with Boegel-EPII after 72 hours of continuous mixing exhibited similar crack growth to that of panels coated with the same Boegel-EPII solution mixed for only 15 minutes. However, the failure modes were only about 85% cohesive. Boegel-EPII solution appeared to provide adequate performance (95% cohesive failure for a nylon-pad-abraded surface) after 24 hours of continuous mixing. This is not recommended due to the cloudy appearance of the solution and the desire to use solution appearance for quality control.

Table 5.8-5: Boegel-EPII Pot-life Evaluation Wedge Test Results

Boegel-EPII Mixing Time	Initial (in)	Cummulative Crack Growth (in)							Failure Mode*
		1 hr	8 hr	24 hr	7 days	14 days	21 days	28 days	
15 minutes	1.13	0.02	0.05	0.07	0.12	0.15	0.17	0.19	97% co
30 minutes	1.16	0.03	0.06	0.09	0.13	0.16	0.16	0.16	96% co
4 hours	1.14	0.05	0.08	0.09	0.14	0.16	0.17	0.18	94% co
8 hours	1.14	0.05	0.09	0.11	0.16	0.19	0.19	0.20	95% co
24 hours	1.21	0.03	0.09	0.10	0.15	0.16	0.18	0.18	95% co
30 hours	1.11	0.04	0.09	0.10	0.16	0.16	0.17	0.19	93% co
48 hours	1.17	0.04	0.09	0.12	0.17	0.19	0.20	0.22	92% co
72 hours	1.17	0.04	0.08	0.10	0.15	0.18	0.18	0.20	85% co

* co: cohesive failure within the adhesive layer
Remaining noncohesive failure occured betweeen the primer and aluminum

5.8.5 Surfactant Study

To obtain a more uniform coating over the surface of the metal, the use of a surfactant was tested in the sol-gel formulation. In previous work, a series of surfactants was screened as to their utility in this application. The ideal surfactant would provide surface leveling and coating

uniformity without affecting adhesion or durability properties. To test this, #220 alumina paper (3M 326U) was used to abrade wedge test adherends to conduct an evaluation of the use of FC-170C surfactant in the Boegel-EPII and its relative performance on abraded 2024-T3 versus 7075-T6 samples. Details of their processing appear in Table 5.8-6. The wedge test results for these samples, conditioned at 140F and >98% RH, are shown in Table 5.8-7. The data indicate there were no significant differences in crack growth between the sanded 2024-T3 samples coated with Boegel EP-II solution with or without FC-170C surfactant.

Table 5.8-6: Surfactant Study Sample Preparation Test Matrix

Sample Number	**Aluminum Alloy**	**Surface Preparation**	**Sol-Gel Formulation**	**Application Method**	**Application Time**
S 7-4	Bare 2024-T3	#220 Alumina Sandpaper Sanded, 3min / Panel / Piece	Boegel EP-II, No Surfactant	Brush	2 minutes
S 7-5	Bare 7075-T6	"	"	Brush	2 Minutes
S 7-6	Bare 2024-T3	"	Boegel EP-II, 0.0018g FC-170C / Liter	Brush	2 Minutes
Sample Number	**Drying Time Before Priming**	**Primer and Batch Number**	**Application Method**	**Adhesive**	**Cure Method**
S 7-4	89 Minutes Air Drying	BR 6747-1	HVLP Spray	AF 163-2M	Autoclave
S 7-5	96 Minutes Air Drying	"	"	"	"
S 7-6	93 Minutes Air Drying	"	"	"	"

Table 5.8-7: Surfactant Study Wedge Test Results

Alloy /Sol-Gel Formulation Used	**Initial (in)**	**Cumulative Crack Growth (in)**						**Failure Mode***
		24 hr	**168 hr**	**336 hr**	**504 hr**	**672 hr**	**1008 hr**	
S 7-4 2024-T3, No Surfactant	1.21	0.10	0.23	0.25	0.26	0.29	0.29	82% co
S 7-5 7075-T6, No Surfactant	1.17	0.10	0.26	0.30	0.30	0.32	0.32	50% co
S 7-4 2024-T3, 0.0018g/l FC-170C Surfactant	1.23	0.10	0.28	0.28	0.30	0.31	0.31	82% co

* co: cohesive failure within the adhesive layer

These results indicate that use of FC-170C cationic surfactant, within the concentration range tested in this study, does not have a deleterious effect on the adhesion or durability of the bonded interface, as evidenced by the Al 2024 specimens. In addition, this surfactant was very effective in improving the coating properties for the sol-gel deposition. However, as discussed previously, FC-170C is no longer a viable product. The poor failure mode results, particularly for the 7075-T6 specimens could be due to the fact this evaluation was conducted before optimal alumina media were determined (3M 326U abrasive papers were not optimal).

5.8.6 Addition of Corrosion Inhibitor to Boegel-EPII Formulation

A test plan (Table 5.8-8) was executed to determine the benefits of adding a corrosion inhibitor to the bondline in a completely ambient-temperature-cure bonded system without primer. Potassium dichromate was used as the active inhibitor to demonstrate feasibility of the concept. Ultimately, a nonchromated inhibitor would be incorporated. EA 9309.3NA paste adhesive was used for bonding. The wedge test panels were cured at ambient temperature (approximately 70°F) under a vacuum bag (23-26in Hg). Glass beads in the adhesive bondline controlled the bondline thickness and a scrim cloth was added to improve consistency. Wedge test results are shown in Table 5.8-9. Specimens were tested at 120°F and 95-100% RH. The specimens were removed early (prior to 1008 hours) due to mechanical failure of the humidity cabinet. The specimens with lower levels of potassium dichromate in the sol-gel layer performed best. All specimens showed adhesional failure at the metal/sol-gel interface after 30 days and 6 weeks of exposure, with the exception of the specimens with 0.1% potassium dichromate incorporated in the sol-gel layer.

Table 5.8-8: Test Plan for EA 9309.3NA Paste Adhesive over Unprimed, Sol-Gel Coated Substrates with Corrosion Inhibitor

Specimen	Substrate	Surface Prep	Abrasion Time	Boegel-EPII
D33-1	2024-T3	Med. Scotch-Brite™	2-3 minutes	Brush. Add 1% Potassium Dichromate
D33-2	2024-T3	Med. Scotch-Brite™	2-3 minutes	Brush. Add 0.5% Potassium Dichromate
D33-3	2024-T3	Med. Scotch-Brite™	2-3 minutes	Brush. Add 0.1% Potassium Dichromate
D33-4	2024-T3	Med. Scotch-Brite™	2-3 minutes	Brush. Add 0.01% Potassium Dichromate

Table 5.8-9: Wedge Test Results for Adding Corrosion Inhibitor to Boegel-EPII Formulation on Nylon-Pad/Sol-Gel

Sol-Gel Used	Initial (in)	Cumulative Crack Growth (in)						Failure Mode*
		24 hr	168 hr	336 hr	504 hr	672 hr	840 hr	
Boegel-EPII with 1% Potassium Dichromate	1.63	0.70	0.90	0.90	0.90	0.95	0.95	0% co
Boegel-EPII with 0.5% Potassium Dichromate	1.63	0.57	0.57	0.75	0.75	0.75	0.75	0% co
Boegel-EPII with 0.1% Potassium Dichromate	1.65	0.65	0.65	0.65	0.65	0.65	0.65	59% co
Boegel-EPII with 0.01% Potassium Dichromate	1.73	0.35	1.03	1.26	1.26	1.26	1.26	0% co

* co: cohesive failure within the adhesive layer

6 SURFACE CHARACTERIZATION

The majority of the sol-gel process development work was focused on identifying the process parameters that could produce repeatable, reliable, long-term durable bonds. Surface characterization was used in order to derive the scientific rationale to help explain and guide the experimental work. The effort focused on surface analysis and sol-gel film properties. Surface analyses of the substrates included analysis of surface morphology and chemistry and their role in the long-term bond durability. The sol-gel film properties assessment investigated changes in the film modulus due to exposure to a typical hot/humid environment.

6.1 Surface Analysis

The surfaces of Al 2024-T3, Al 7075-T6, Ti 6Al-4V, and stainless steel have been evaluated for surface roughness. Some findings and conclusions that can be ascertained from the surface roughness measurements in are listed below:

- The roughness average value (R_a) increases with the use of coarser abrasive media,
- The mean spacing values between profile irregularity increases with the use of coarser abrasive media,
- The average spacing of the local peaks of the profiles increases using coarser abrasive media, and
- The developed profile length that would be obtained from drawing out the profile in a straight line increases using coarser abrasive media.

Abrasive blasting is a good process because it 1) increases roughness; 2) uniformly increases mean spacing and average spacing of the profile irregularities; and 3) increases the developed profile length. More aggressive abrasive methods may create a surface that is too rough and may actually be detrimental. If the peaks and valleys are too large, the sol-gel and adhesive may not flow into the valley areas, thus leaving them open and unprotected where moisture may travel, accumulate, and initiate corrosion in the bonded joint.

Al 2024-T3 surfaces that were grit blasted had surface roughness (Ra) values of 16 microinch (μin) for 50-micron size (#280) alumina grit and 24μin for 80-micron size (#180) alumina grit. Chemical analyses of these samples are given in Table 6.1-2. All data are the average of three samples. Observations include:

- The percentage of aluminum consistently decreases by after grit blasting.
- Silicon, Oxygen, and Iron concentrations increase after grit blasting. The increase in oxygen is primarily due to the fact that aluminum oxide grit particles are being embedded into the substrate and thus increasing the overall oxygen concentration and decreasing the effective amount of aluminum that is being analyzed.
- The concentration of zinc remains relatively constant.
- There are also differences in the copper concentration before and after grit blasting that indicate the intermetallic particles may be breaking up and redistributing themselves over the sample surface.

Table 6.1-1:Sample Surface Roughness Data for Al 2024-T3

Surface Preparation	$R_{a\ (min)}$	I_r
(1) - MEK Wipe	6.5	1.008
(2) – Brulin 815GD, Turco 2623	6.9	1.008
(3) - Brulin, Turco, Boeclene	7.8	1.0029
(4) - Brulin, Turco, #180 Alumina Grit Blast	38.9	1.0351
(5) - Brulin, Turco, #220 Alumina Abrading	16.8	1.0037
(6) - Brulin, Turco, VFN Blue Scotch-Brite™	16.1	1.0065
(7) - Brulin, Turco, MED Maroon Scotch-Brite™	58.4	1.0287
(8) - Brulin, Turco, CRS Brown Scotch-Brite™	75.3	1.0324
(9) - Brulin, Turco, PAA	11.5	1.0077
(10) - Acetone Wipe	19.2	1.0096
(11) - Acetone Wipe, #180 Grit Blast	26.6	1.0200
(12) - Acetone Wipe, Scotch-Brite™	34.3	1.0177
(13) - Acetone Wipe, #120 Alumina Abrading	37.6	1.0133

R_a: roughness average value
I_r: profile length ratio (the ratio of the developed profile length to the sample length)

Table 6.1-2: Chemical Analysis of Grit-Blasted Al 2024-T3

Samples	Al	Si	O	Mg	Zn	Mn	Fe	Cu
As received	92.88	0.00	1.07	1.70	0.14	0.44	0.06	3.78
After #180 alumina grit blasting (samples show large trench size topographies	91.84	0.37	2.07	1.31	0.13	0.32	0.08	3.82
As received	93.52	0.05	0.78	0.78	0.17	0.50	0.06	3.58
After #280 alumina grit blasting (samples show small trench size topographies	87.38	0.67	6.36	1.52	0.17	0.37	0.10	3.45
As received	93.14	0.08	0.81	1.54	0.15	0.53	0.02	3.73
After #280 alumina grit blasting	88.89	0.27	4.74	1.40	0.13	0.41	0.09	4.10

The chemical analyses for 7075-T6 aluminum blasted with #180 alumina grit and #280 alumina grit are presented in Table 6.1-3.

- Aluminum concentration decreases by approximately 4%.
- As with 2024-T3 the percent Silicon, Oxygen, and Iron concentrations increase after grit blasting. The increase in oxygen is primarily due to the embedded grit as stated before.
- The concentration of zinc decreases modestly for 7075-T6 samples.
- Magnesium concentrations decrease while copper concentrations increase.

Table 6.1-3: Chemical Analysis of Grit-Blasted Al 7075-T6

Samples	Cu	Cr	Ti	Fe	Mn	Zn	Mg	Al	Si	O
As received	1.79	0.29	0.06	0.09	0.07	7.18	3.30	83.41	0.03	3.77
#180 alumina grit	1.91	0.20	0.17	0.16	0.10	7.14	2.5	79.32	0.83	7.68
As received	1.80	0.22	0.02	0.05	0.08	6.68	3.14	84.95	0.04	3.01
#280 alumina grit	2.68	0.20	0.15	0.16	0.06	5.93	2.20	80.62	0.17	7.30

The biggest difference between the before and after grit-blasting samples is the change in percent oxygen. Both substrates showed large increases in oxygen content that can be attributed to the grit (Al_2O_3) that becomes embedded in the substrate during the process.

Abrading a sample with alumina paper, as opposed to grit blasting, results in a completely different chemical make-up on the surface. The major difference between abrasion and grit blasting is the concentration of aluminum increases while the concentration of oxygen decreases. In the case of 2024-T3 the oxygen concentrations are reduced to near zero. This along with the morpohology may be key to identifying the characteristics of a durable bond.

6.2 Gloss Meter Measurements

To give a semiquantitative idea of the degree of surface roughness that is achieved using the various mechanical deoxidation processes, a gloss meter was employed to see if the level of gloss and degree of mechanical treatment could be correlated. Several of Al 2024-T3 panels were cleaned and/or mechanically deoxidized using different methods, as described in Table 6.2-1. The testing was performed on mill-annealed sheet as supplied from the vendor. Actual hardware surfaces to be bonded may be formed from other types of stock with different surface finishes.

Table 6.2-1: Gloss Meter Measurements for Various Pretreatments on Al 2024-T3

Sample #	Pretreatment	Angle of Measurement on Gloss Meter		
		20°	60°	85°
R29-1	MEK solvent wiped, bare	>200	>200	128.5
R29-2	#180 alumina grit-blasted, bare	1.4	4.2	4.6
R29-3	Brulin 815GD degreased, Turco® 2623 alkaline cleaned, and Boeclene etched, bare	196.6	>200	130.4
R29-4	0.005” stainless steel wire wheel abraded, bare	18.7	94.1	40.0
R29-5	#240 alumina flapwheel abraded, bare	37.0	150.0	84.7
R29-6	#220 alumina paper abraded, bare	26.1	95.5	35.1
R29-7	#400 SiC paper abraded, bare	14.0	64.1	38.2
R29-8	#600 SiC paper abraded, bare	10.1	46.1	32.3
R29-9	#1500 SiC paper abraded, bare	53.6	126.1	110.5

6.3 X-Ray Absorption Spectroscopy (XAS)

X-Ray Absorption Spectroscopy (XAS) measurements of sol-gel coatings, including extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES), were conducted at the Stanford Synchrotron[29]. Of particular interest were the nature of the chemical bonding and the effect of selected process variations. XAS is ideally suited for these measurements since it is sensitive to coordination number, bond length, disorder, valency, and site symmetry in these amorphous materials.
XANES has been shown to be sensitive to the site symmetry and coordination of the absorbing atom. Several standard zirconium-containing reference compounds were analyzed to model the different coordination sites possible for this atom. It can be postulated, using the standard reference compounds as a guide, that the sol-gel coatings exhibit a doublet feature since their XANES have a large fraction of Zr in network-forming octahedra that are joined primarily at the corners. It appears that the Zr is not in such a site unless the silane component is present and both are on a metal substrate. The plots indicate that Zr is found in a mix of 6-fold and 8-fold sites. The plots also indicate that the valency of the Zr in the sol-gel coatings is approximately 3+. Close examination shows a chemical shift of the position of the Zr K-edge when the sol-gel solution is deposited on a metal substrate.

EXAFS results indicated that sol-gel powders (that had been deposited on polyethylene, removed, and ground up, but never deposited on a metal surface) have a longer Zr-O bond length, which implies coordination numbers of 7 or 8. Coatings formulated from TPOZ alone, without any GTMS, deposited on a metal surface also show a longer Zr-O bond. When both the Zr and Si components are used and the sol-gel is deposited on a titanium surface, the Zr-O bond length shortens.

A peak exists for specimens with sol-gel deposited on a titanium surface that does not occur in the free sol-gel polymer. This analysis was used to infer the presence of a Zr-O-Ti bond in the sol-gel. More analysis is necessary to verify the presence of this bond.

Sol-gel coating samples that were cured in air at RT or at 255°F were examined. The XANES and EXAFS data suggest only subtle differences between these methods of curing and indicate that the bonding at the Zr is essentially the same.

Investigations of aged specimens of sol-gel coated titanium samples that had been left under ambient conditions for over a year indicate no great differences in the first neighbor coordinating atoms.

6.4 Infrared Spectroscopy Characterization Study

Boegel-EPII and coated panels were analyzed using FTIR spectroscopy. There were several goals for this initial characterization effort: 1) to determine whether the epoxy linkage in the organosilane component could be observed during the processing; 2) to ascertain the fate of this functionality over the course of the processing; and 3) to learn what was happening to the chemistry of the coating, and network formation, during curing at both room temperature and elevated temperatures. Understanding the aging characteristics of the sol-gel solution and the structure/property changes in the deposited sol-gel coating would help determine conditions to specify in the process documents.

6.4.1 Sol-Gel Chemistry Evaluation

The basic Boegel-EPII solution (without surfactant) contains γ-glycidoxypropyltrimethoxysilane (GTMS), zirconium n-propoxide (TPOZ), n-propanol (the TPOZ solution contains 25% n-propanol and TPOZ hydrolyzes to produce n-propanol), glacial acetic acid (GAA), methanol (produced during the hydrolysis of the GTMS), and water. Due to its makeup, the solution was evaluated to see if it posed a VOC problem. It was determined there is no VOC issue with Boegel-EPII[30]. Currently, the solution is formed by adding a TPOZ/GAA solution to the hydrolyzed silane. A premixed solution of TPOZ, GAA, and water is currently being considered as one component for a two-component kit, so an FTIR scan of the solution was conducted. Two additional Boegel-EPII solutions and two Boegel-EPII-deposited coatings were also analyzed:

(1) **Boegel-EPII Solution, Unaged**
The basic Boegel-EPII solution was aged 15 minutes (after the 30-minute induction period) prior to scanning. A water blank was used to correct for the presence of water in the sample (automatically subtracts the absorbance due to water).

(2) **Boegel-EPII Solution, Aged 4 weeks**
The same Boegel-EPII solution used for the unaged scan was rescanned after aging for 4 weeks. As before, a water background was used to remove the water absorptions.

(3) **Boegel-EPII-Deposited Coating, Dried at Ambient Temperature**
An Al 2024-T3 bare panel was treated with Boegel-EPII (solution age 30 minutes) then air-dried 30 minutes prior to scanning. An aluminum blank was used to remove the background.

(4) **Boegel-EPII-Deposited Coating, Cured at 250°F**
An Al 2024-T3 bare panel prepared as above with the addition of a 30-minute cure at 250°F prior to FTIR analysis. As before, an aluminum blank was used to remove the background.

Interpretation of the infrared spectra, not a simple matter, is described below. Absorption bands may be obscured by overlapping bands. In addition, the absorption bands of a particular group may be shifted by various structural features, such as electron withdrawal by a neighboring group and hydrogen bonding (particularly a problem in aqueous solutions). All of the peaks in the pattern are really a composite of absorption bands from all of the components. Therefore, the peak identifications only show the species with the major absorption in that area of the spectrum.

Most of the peaks in the FTIR patterns have been identified. However, a number of smaller peaks (particularly in the region of 1600 cm^{-1} to 1200 cm^{-1}) were not identified. These bands are in the fingerprint region and are due to a number of different potential absorbencies.

6.4.2 Characteristic Group Frequencies

The characteristic group frequencies for methanol, silicon-oxygen-silicon (Si-O-Si), epoxide, and silicon bonded to a methoxy group ($Si-OCH_3$) are summarized in Table 6.4-1.

Table 6.4-1: Characteristic Group Frequencies

Species	Characteristic Absorbencies (cm-1)
Methanol	2950, 2840, 1460-1420, 1120, 1030 - 1015 Strong
Si-O-Si	1100 - 1000
Epoxide	3059, 2999, 1479, 1256, 914, 851

6.4.3 TPOZ/GAA/H_2O Premix

The initial FTIR scan of the TPOZ/GAA/H_2O solution is shown in Figure 6.4-1 and Figure 6.4-2.

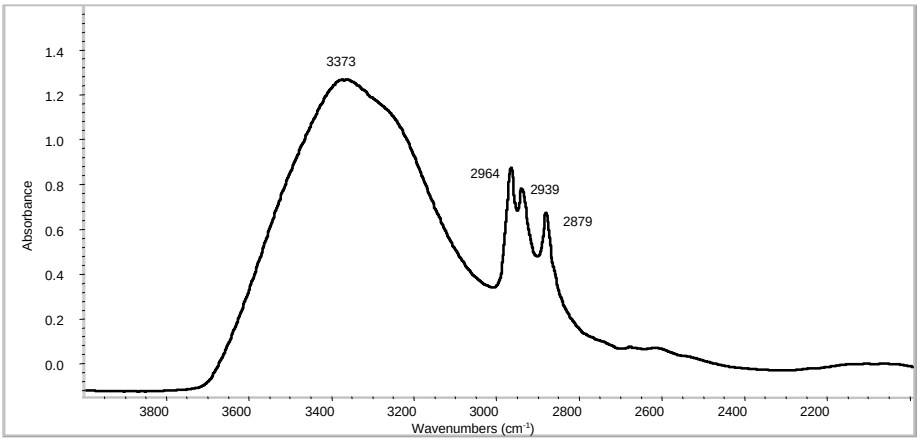


Figure 6.4-1: TPOZ/GAA/H_2O initial scan (4000cm^{-1} - 2000cm^{-1})

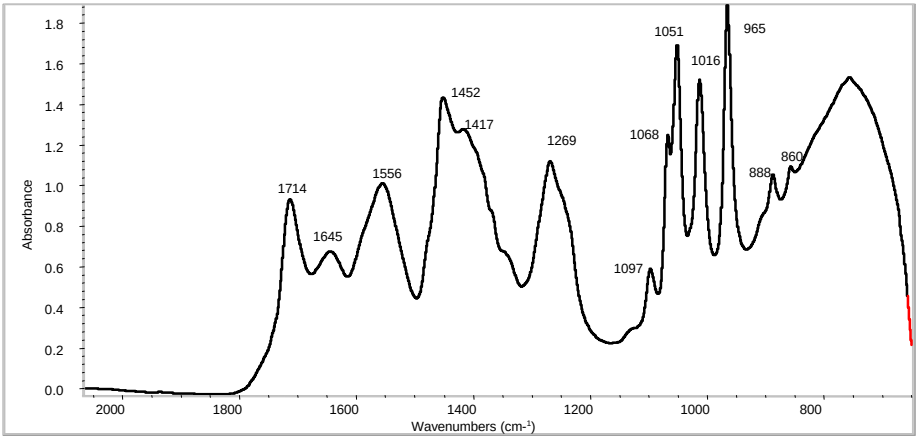


Figure 6.4-2: TPOZ/GAA/H_2O initial scan (2000cm^{-1} - 650cm^{-1})

The relative peak intensity (A/Ao) is a percentage of the peak height relative to the maximum absorption in the pattern. The value is commonly used to index a spectrum. However, care must be exercised when interpreting the data, as changes in background or peaks located on the

shoulders of other peaks will affect the values. The FTIR pattern and the identified absorbing species for the TPOZ/GAA/H_2O solution are presented in Table 6.4-2.

Table 6.4-2: FTIR Pattern for TPOZ/GAA/H2O Solution

Frequency cm^{-1}	**A/Ao**	**Species**
3373	67	OH from H_2O and n-propanol
2964	46	CH_3 out of phase
2939	41	CH_2 out of phase
2879	36	CH_3 in phase
1714	49	CH_3COOH undimerized, carbonyl stretch
1645	36	H_2O scissoring
1556	53	$CH_3CO_2^-$ salt, CO_2 out of phase stretch
1452	76	CH_3 out of phase, CH_2 scissoring
1417	68	n-propanol, OH in phase, CO_2^- in phase stretch
1269	59	C-O (carbon single bond to oxygen from GAA)
1097	31	n-propanol
1068	66	n-propanol
1051	91	n-propanol
1016	74	n-propanol
965	100	n-propanol
888	56	n-propanol
860	56	n-propanol

With the exception of the CH_3 and CH_2 absorptions, no bands were identified as resulting from zirconium compounds. This was not unexpected, as the zirconium mole fraction is around 5%.

6.4.4 Boegel-EPII Solution

FTIR scans of the unaged Boegel-EPII solution are shown in Figure 6.4-3 and Figure 6.4-4.

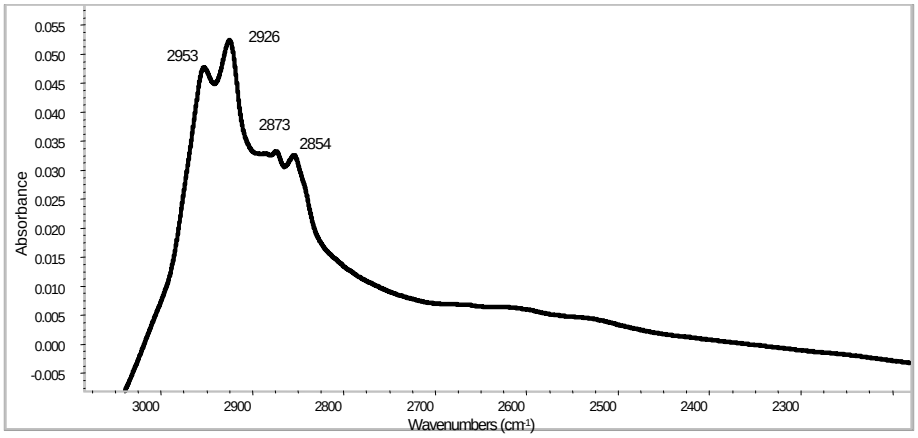


Figure 6.4-3: Unaged Boegel-EPII Solution (3100cm^{-1} - 2100cm^{-1})

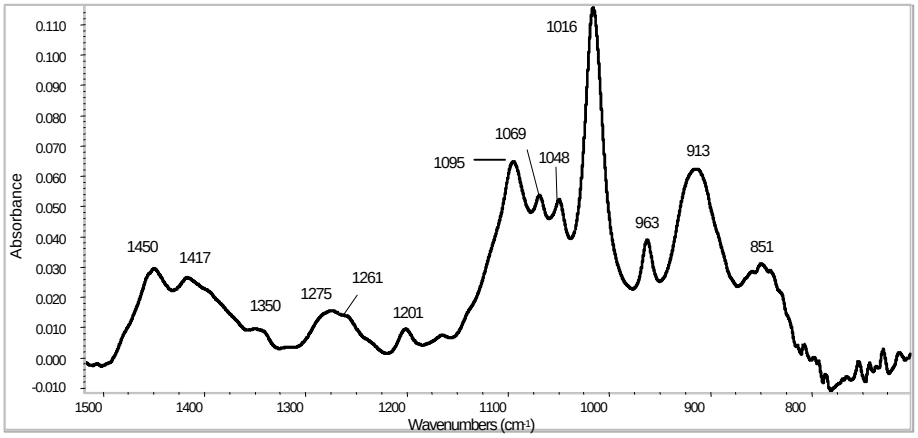


Figure 6.4-4: Unaged Boegel-EPII Solution (1500cm^{-1} - 650cm^{-1})

The epoxide group can be seen in several of the bands (1261, 913 and 851cm^{-1}). The peaks at 913 and 851cm^{-1} are the most visible and are particularly important. The noncyclic ether peak is at 1095cm^{-1}. Methanol from the hydrolysis of the GTMS is evident in two peaks (1417 and 1016cm^{-1}). No peaks could be identified that could be assigned to the methoxy protection groups. In addition, work on other silanes with methoxy protection groups has shown that the strongest methoxy absorbencies (in a water-alcohol solution) are at 1192, 1061 and 807cm^{-1}. The 1192 and 807cm^{-1} bands are missing from the pattern. Therefore, it is believed that the methoxy groups have been hydrolyzed.

The FTIR scan of the aged GTMS-based sol-gel solutions are shown in Figure 6.4-5 and Figure 6.4-6.

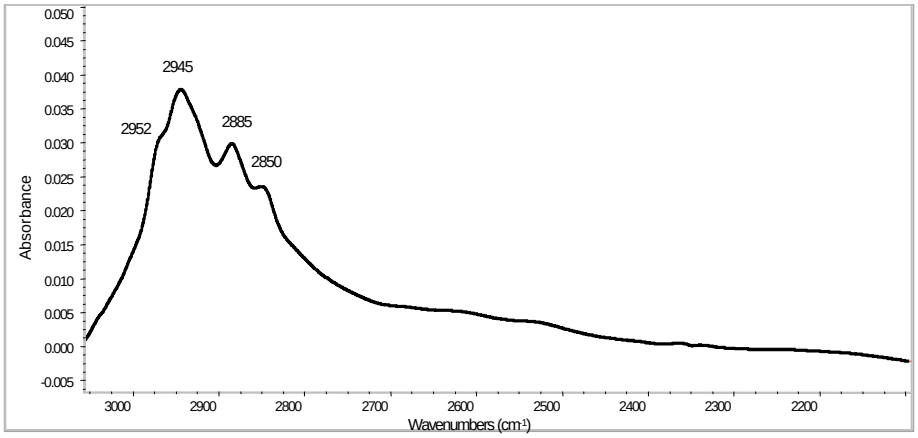


Figure 6.4-5: Boegel-EPII Solution Aged 4 Weeks (3100cm^{-1} - 2100cm^{-1})

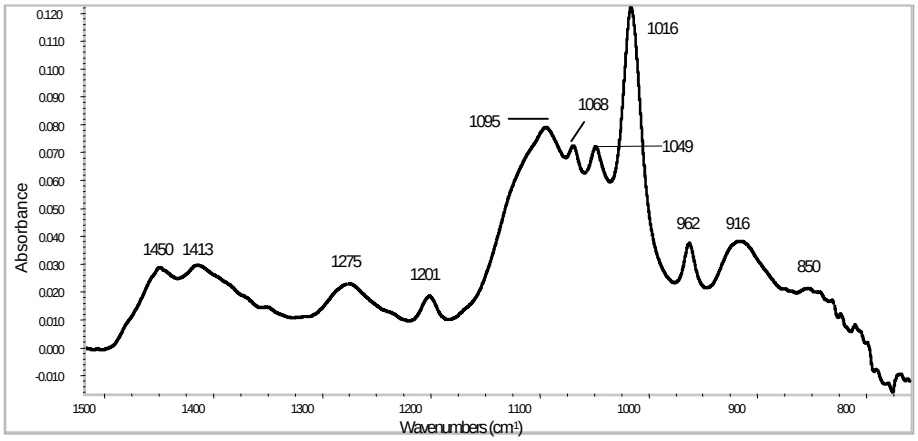


Figure 6.4-6: Boegel-EPII Solution Aged 4 Weeks (1500cm^{-1} - 650cm^{-1})

After aging, the epoxide bands at 1261, 916 and 850cm^{-1} became significantly smaller. The amount of FTIR radiation absorbed is directly related to the total number of bonds responding to that particular frequency. This makes the absorption directly related to the molar concentration. Therefore, the reduction in the epoxide peak area indicates a decrease in the epoxide concentration. In addition, the CH_2 peaks at 2945 and 2885cm^{-1} are different and indicate a new type of CH_2 group that formed when the epoxide ring opened. The peak for the noncyclic ether remained relatively constant, and that ether appears to be stable under these conditions.

The FTIR patterns and the identified absorbing species for both the initial and aged sol-gel solutions are presented in Table 6.4-3.

Table 6.4-3: FTIR Pattern for Boegel-EPII Solutions

Initial Solution		**Aged Solution**		**Species**
cm^{-1}	**A/Ao**	**cm^{-1}**	**A/Ao**	
2953	41	2952	30	CH_3
2926	45	2944	31	CH_2
2873	29	2885	24	CH_3
2854	28	2850	19	CH_2
1450	25	1450	23	CH_3, CH_2
1417	23	1414	24	OH in plane (methanol)
1350	8	1352	12	
1275	13	1275	18	
1261	12	***	***	C-O stretch (epoxide)
1201	8	1201	15	
1165	6	***	***	
1095	56	1095	64	C-O-C (non-cyclic ether)
1069	46	1068	59	n-propanol
1048	45	1049	59	n-propanol
1016	100	1016	100	C-OH (methanol)
963	28	962	28	n-propanol
913	53	916	31	epoxide (out of phase)
851	27	851	17	epoxide (out of phase)

6.4.5 Boegel-EPII-Deposited Coatings

The FTIR scan of the room temperature (RT) dried Boegel-EPII panel is shown in Figure 6.4-7 and Figure 6.4-8.

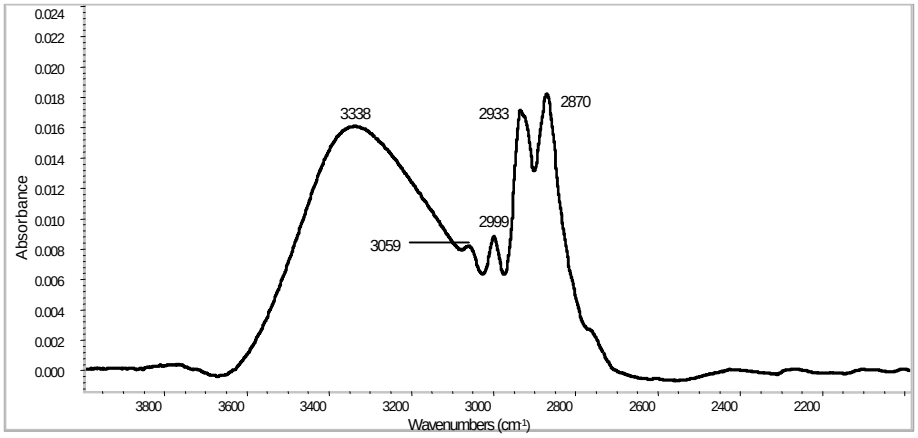


Figure 6.4-7: RT-Dried Boegel-EPII Panel (4000cm^{-1} - 2100cm^{-1})

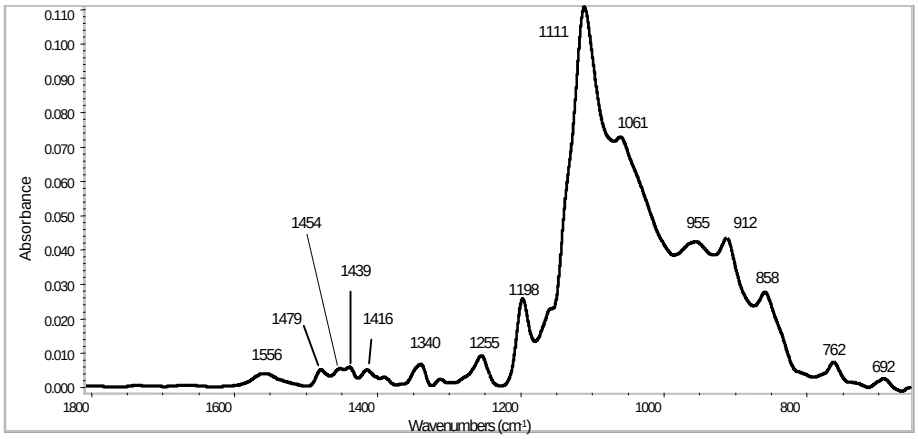


Figure 6.4-8: RT-Dried Boegel-EPII Panel (1800cm^{-1} - 650cm^{-1})

The FTIR scan for 250°F-cured Boegel-EPII panel is shown in Figure 6.4-9 and Figure 6.4-10.

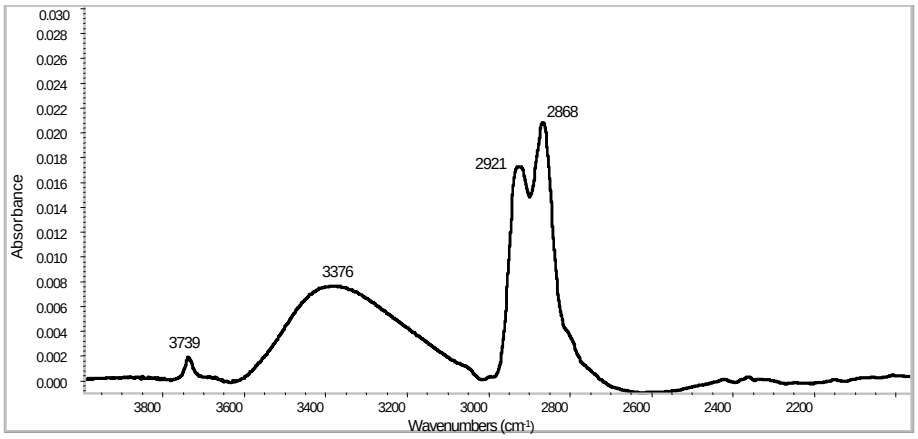


Figure 6.4-9: 250°F-Cured Boegel-EPII Panel (4000cm^{-1} - 2100cm^{-1})

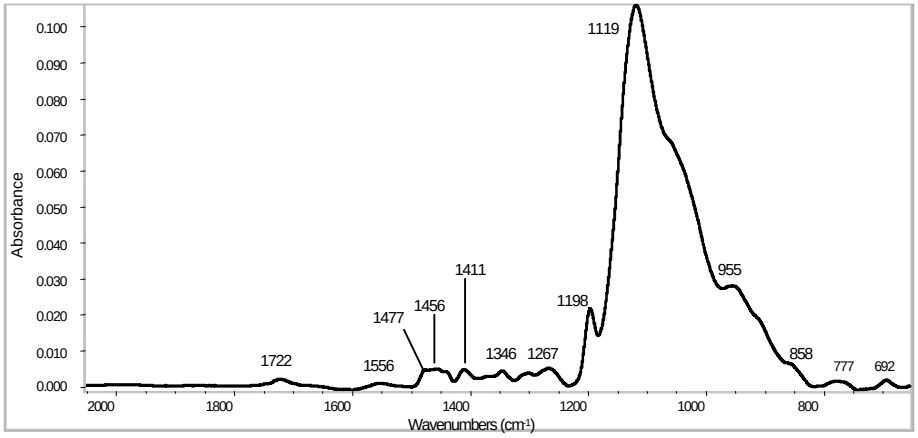


Figure 6.4-10: 250°F-Cured Boegel-EPII Panel (2100cm^{-1}- 650cm^{-1})

The FTIR patterns and the identified absorbing species for the cured and noncured panels are presented in Table 6.4-4.

In the RT-dried absorption spectrum, the large broad peak at 3338cm^{-1} is due to hydrogen-bonded OH groups (most likely Si-OH and H_2O). The epoxide group has a large number of peak assignments (3059, 2999, 1479, 1255, 912 and 858cm^{-1}). The peaks at 1111, 1061 and 955cm^{-1} indicate that the Si-O-metal bond formed prior to curing. There were no peaks identified that resulted from either acetic acid or the alcohols, indicating the solvents were completely flashed off during the 30-minute air drying. However, there was a peak at 1556cm^{-1} that was due to a metal acetate (acetic acid salt). An acetate peak was also identified at 1416cm^{-1}. The peak at 1198cm^{-1} is unknown. The wave number matches the methoxy peak. However, it is believed the GTMS was hydrolyzed prior to application of the solution.

Table 6.4-4: FTIR Pattern for Boegel-EPII Panels

Non-Cured Panel		Cured Panel		Species
cm^{-1}	A/Ao	cm^{-1}	A/Ao	
***	***	3739	2	$Metal^{+}$, OH^{-}, nonhydrogen-bonded
3338	14	3376	7	OH hydrogen bonded (H_2O, Si-OH)
3059	7	***	***	epoxide
2999	8	***	***	epoxide
2933	15	2921	16	CH_2
2870	16	2868	26	CH_2
***	***	1722	2	COOH in solution (acetic acid)
1556	4	1556	1	$Metal^{+}$, CO_2^{-} (salt of GAA)
1479	4	***	***	epoxide
***	***	1477	4	CH_2
1454	5	1456	5	CH_2
1439	5	1442	4	CH_2
1416	4	1411	4	CO_2- (in phase)
1390	2	***	***	
1340	6	1346	4	
1313	2	1302	3	
***	***	1267	5	
1255	8	***	***	epoxide
1198	23	1198	20	Si-OCH_3 ?
1111	100	1119	100	C-O-C, Si-O-Metal
1061	66	***	***	Si-O-Metal
955	38	955	26	Si-O-Metal
912	39	***	***	epoxide
858	24	858	6	epoxide
762	6	777	1	
692	2	692	2	

In the 250°F-cured spectrum, there is a nonhydrogen-bonded metal hydroxide peak at 3739cm^{-1} and a broad hydrogen-bonded hydroxide peak at 3376cm^{-1} (most likely Si-OH). The CH_2 bands at 2921 and 2868cm^{-1} were identified as CH_2-O. There is a new peak at 1722cm^{-1} that is the result of COOH. There is also a metal acetate peak at 1556cm^{-1} and an acetate peak at 1411cm^{-1}. Therefore, it is quite certain there is a COOH functionality on the surface of the cured panels. Most likely, the COOH formed from the metal acetate identified in the noncured pattern. In addition, there was a reduction in the epoxide concentration. This can best be seen in the peaks at 3059 and 2999cm^{-1}.

6.5 Incorporation of Dyes into Sol-Gel Coatings

The incorporation of visible dyes into the sol-gel formulation was studied as a means of providing a quality control technique to determine whether the sol-gel has been applied to the surface of a metal. In the initial studies, screening was conducted on a variety of dyes to determine whether the chemistries of the dyes were compatible with the sol-gel chemistry. Dyes

were added to the sol-gel solution and the resulting coating applied to an aluminum substrate to determine which dyes produce a visually discernible sol-gel coating.

6.5.1 Sample Preparation

Dyes were used at a concentration of approximately two to four grams per liter. One hundred milliliters of each dyed sol-gel solution was formulated for each test batch. The dye concentration was 5% of the active sol-gel components: GTMS and TPOZ): 0.05(2g GTMS/100ml sol-gel solution + (0.75)1g TPOZ/100ml sol-gel solution) = 0.1375g dye/100ml sol-gel solution.

Dye was added directly to the sol-gel solution at room temperature. All dyes, except for test #10, were powders and were predissolved by diluting with water in a bottle and shaking. All solutions were vividly colored, although it was evident that not all dyes were completely dissolved. Dyed solutions were allowed to sit for approximately one hour while the substrates were being prepared. The substrates for this test were 4-inches x 6-inches x 0.040inch 2024-T3 bare aluminum. Panels were aqueous degreased (Brulin Formula 815GD) and alkaline cleaned (Isoprep 44). Panels were then abraded using 3M #220 grit aluminum oxide paper on an orbital sander. The sol-gel solutions were shaken immediately prior to application. Substrates were brush coated using a 1-inch natural bristle varnish brush. Several passes of sol-gel were completed during a two-minute wetting period. Panels were placed vertically in a rack and allowed to dry overnight under ambient conditions.

6.5.2 Dyed Panel Analysis

A subjective scale of A, B, and C was adopted to show the degree of solubility of the dyes after the dyed sol-gel solutions dried overnight. A visual judgment was made by looking at the amount of dye that appeared to be in the bottom of the test bottle. “A” indicates no visible solids, “B” indicates a small amount of solid, and “C” indicates significant solids. The 10-hour pot-life for the mixed sol-gel solution had expired several hours prior to conducting this analysis.

A subjective scale of A, B, and C was adopted for the application process to indicate the ease of application and the appearance of the panels during application. “A” indicates the best-looking specimens and “C” refers to the worst-looking specimens. Some of the solutions had a significant amount of undissolved particles. These particulate-laden solutions were then applied onto the panels resulting in an uneven coating. Several solutions were frothy, and foam was present when the solution was applied onto the substrate resulting in degradation of coating uniformity.

Results from the initial dye incorporation study are shown in Table 6.5-1. Comments on the appearance of the sol-gel-treated panels after drying overnight are made within the table. Based on appearance of the substrate, the following dyes were chosen for further evaluation: Bordeaux #4, Yellow #2, Orange No. 4, Sanodal Turquoise Liquid, and Specialty Blue #1. Wedge tests were conducted on these selected specimens to assess the effect of the incorporated dyes on the adhesion and durability of the bonded system. The results are shown in Table 6.5-1.

Table 6.5-1: Results of Dye Incorporated Sol-Gel Coatings

Test	Dye Name	Vendor	Solubility	Application	Panel Appearance
0	Control (no dye)	none		A+	Clear.
1	Specialty Blue No. 10	US Specialty Color Corp.	C-	C	Slight darkening, many undissolved particles.
2	AC-2 Red	Aldoa Co.	B+	C	Very red, wave lines around undissolved particles.
3	Chromate Brown No. 2	Clariant Corp.	B	B-	Slight brown, some undissolved particles.
4	Chromate Bordeaux No. 4	Clariant Corp.	B+	B+	Red hourglass drying pattern, some wave lines.
5	Chromate Orange No. 1	Clariant Corp.	A	B	Very light color, consistent, even-looking coating.
6	Chromate Yellow No. 2	Clariant Corp.	B+	B	Light color, consistent, even-looking coating.
7	Chromate Orange No. 2	Clariant Corp.	C	B	Very light color, clearer around top and sides.
8	Chromate Orange No. 4	Clariant Corp.	A	B	Light color, consistent, even-looking coating.
9	Chromate Blue No. 1	Clariant Corp.	B	B-	Light blue color, undissolved particles and wave lines.
10	Sanodal Turquoise	US Specialty Color Corp.	A-	A	Blue hourglass drying pattern, few particles.
11	Specialty Aurous 19	US Specialty Color Corp.	A	B+	Very light color, mottled appearance.
12	Specialty Blue No. 1	US Specialty Color Corp.	B+	B+	Blue color, clear around top and edges.
13	Specialty Green No. 2	US Specialty Color Corp.	B	C	Light blue color, many undissolved particles.
14	Specialty Yellow No. 2	US Specialty Color Corp.	A	C	Yellow color, clear around top and sides, dark at bottom.
15	Specialty Orange No. 7	US Specialty Color Corp.	C-	C	Orange color, very dark at bottom.

Figure 6.5-1: Wedge Test Performance of Sol-Gel Coatings with Selected Incorporated Dye

Surface Preparation	Initial (in)	Cumulative Crack Growth (in)					
		1 hr	24hr	168hr	336hr	672hr	1008hr
Control (no dye)	1.21	0.03	0.11	0.19	0.19	0.21	0.21
Chromate Bordeaux #4	1.20	0.01	0.16	0.23	0.23	0.26	0.26
Chromate Yellow #2	1.20	0.01	0.15	0.17	0.20	0.20	0.20
Chromate Orange #4	1.22	0.00	0.13	0.17	0.20	0.20	0.20
Sanodal Turquoise	1.16	0.00	0.17	0.25	0.25	0.25	0.25
Specialty Blue #1	1.24	0.00	0.17	0.32	0.32	0.34	0.34

Table 6.5-2: Wedge Test Performance for Sol-Gel Coatings with Selected Incorporated Dyes

Surface Preparation	Initial (in)	Cumulative Crack Growth (in)					
		1 hr	24hr	168hr	336hr	672hr	1008hr
Control (no dye)	1.21	0.03	0.11	0.19	0.19	0.21	0.21
Chromate Bordeaux #4	1.20	0.01	0.16	0.23	0.23	0.26	0.26
Chromate Yellow #2	1.20	0.01	0.15	0.17	0.20	0.20	0.20
Chromate Orange #4	1.22	0.00	0.13	0.17	0.20	0.20	0.20
Sanodal Turquoise	1.16	0.00	0.17	0.25	0.25	0.25	0.25
Specialty Blue #1	1.24	0.00	0.17	0.32	0.32	0.34	0.34

The wedge crack growth data show only one of the dyes, Specialty Blue #1, appeared to severely degrade performance. Three of the dyes contain Cr^{3+}, so they were eliminated for consideration in further testing since their incorporation into the sol-gel solution would prevent it from being chromate-free. That left one dye, the Sanodal Turquoise, as a potential agent for incorporation to facilitate quality control (QC) analyses. Failure modes for the wedge test specimens are shown in Table 6.5-3. Failure analyses indicate the Sanodal Turquoise also degrades the performance of the bonded specimen. Since one of the dyes were found to be acceptable, work with dyes was discontinued.

Table 6.5-3: Failure Modes for Incorporated Dye Specimens

Specimen #	Dye	Failure Mode
010306-1	None	93% cohesive*
010306-2	Chromate Bordeaux #4	92% cohesive
010306-3	Chromate Yellow #2	94% cohesive
010306-4	Chromate Orange #4	91% cohesive *
010306-5	Sanodal Turquoise Liquid	78% cohesive
010306-6	Specialty Blue #1	14% cohesive

* some observable primer-to-adhesive failure

7 CONCLUSIONS

7.1 General

The SERDP PP-1113 effort successfully developed and initiated transition of new metal surface preparations based on sol-gel technology for adhesive bonding. Multiple processes were developed using the same chemical formulation with alternate pretreatment, application, and post-treatment steps. These similar approaches yield bond strength and moisture durability performance that are equivalent to or better than currently approved procedures for a variety of field-level and depot/production applications for aluminum, titanium, and steel alloys. The waterborne sol-gel chemistry, designated as Boegel-EPII, is currently commercially available in four-component kits from Advanced Chemistry & Technology (Garden Grove, CA) under the product name AC-130. Upon completion of work to address issues pertaining to end-user environments, to be conducted in a follow-on effort (ESTCP Project PP-0204), it is almost certain that multiple variants of the new technology will be implemented for repair bonding for both military and commercial aircraft. Some implementation has already occurred, primarily for adhesive bonding of titanium and stainless steel in the production setting and on-component repair of aluminum.

7.2 Aluminum Alloys

The majority of the development and testing focused on repair bonding of 2024 and 7075 aluminum alloys, particularly the surface activation requirements prior to sol-gel application. A small molecular modeling effort aided somewhat in the development of surface activation techniques, but most of the development and optimization work was driven by empirical testing. The main test method employed was the wedge test (ASTM D 3762) because it is a way to quickly assess the all-important moisture durability performance of bonded joints which is largely attributable to surface preparation. Depending on the application, the tests were conducted at either 120°F or 140°F, both with greater than 95% relative humidity. To be meaningful, wedge test data with the new processes were compared to similar data for existing, approved surface preparation processes. Additional coupon-level mechanical tests were conducted to assess initial bonded joint strength.

Procedures that included aluminum oxide grit-blasting and subsequent primer application (see Appendix) performed as well as the best existing processes. The use of grit-blasting created very robust surface treatments that were tolerant of variables in other processing steps. Variables evaluated included: 1) preabrasion degreasing; 2) sol-gel application method and dwell time on the metal surface; 3) sol-gel dry time and dry method; and 4) primer type, application method, and cure cycle. In addition, multiple metal alloys and epoxy adhesives were assessed during the project and found to be compatible with the new treatments.

Since grit-blasting is not ideal for on-aircraft processing, significant effort was expended toward developing processes using alternate surface activation procedures. Viable processes using a variety of abrasives, including Scotch-Brite™ nylon pads and several “sandpapers,” were developed and tested. Although their performance and repeatability did not equal those of grit-blast/sol-gel, these approaches yielded bonded joint performance as good or better than most existing processes for on-aircraft repair. The processes evaluated were quite simple and feasible

for on-aircraft work. Some included brush-on primer application for use with elevated-temperature-curing film adhesives and others eliminated the priming step for ambient-temperature processing with two-part paste adhesives. The latter approach completely removed hexavalent chromium from metal prebond processing. This simple no-prime method did result in reduced moisture durability, as indicated by the wedge test, compared to the best aluminum prebond treatments. However, its initial strength performance was excellent, and moisture durability far exceeded that provided by the processes currently utilized for many on-aircraft repairs. In fact, when used with certain adhesives, the simple nongrit-blast process without primer performed nearly as well as the current best-practice aluminum preparations that are typically too difficult to employ for on-aircraft work.

7.3 Titanium

Titanium processes, similar to those developed for aluminum, were optimized and tested using Ti-6Al-4V. Many of the existing, approved production titanium prebond surface preparations tend to yield inconsistent results, and the on-component versions (no immersion tank) are even more difficult to control. For these reasons, the new sol-gel surface preparations will be of great benefit for titanium bonding applications and should even enable increase use of bonded titanium. As was the case for aluminum, pretreatment surface activation was the focus of the effort. Chemical immersion tank and alumina grit-blast deoxidation methods resulted in consistently good bonded joint strength and moisture durability performance that was superior to those of approved processes. Due to these good results and the inconsistency of existing processes, several titanium bonding applications using sol-gel preparations have been implemented in the production environment at Boeing. Evaluations of nongrit-blast alternatives show it is more difficult to achieve acceptable moisture durability with these methods for titanium than it was for aluminum alloys.

7.4 Stainless Steel

Few acceptable options exist for prebond treatment of stainless steel alloys. In the production environment, these typically involve strong acid etches. For on-component work, grit-blasting is usually the only viable approach. None result in exceptional long-term moisture durability performance, and initial bondline strengths are often degraded due to failures at the metal interface. For these reasons, few structural bonding applications exist for stainless steel in the aircraft industry. Grit-blast/sol-gel processes were evaluated on 301 and AM355 stainless steels and found to provide excellent moisture durability and bond strength. Separate work has shown promise for alloy and carbon steels, so new steel adhesive bonding applications could be generated due to the results of this project.

7.5 Additional Evaluations

Work was conducted in several additional areas in order to optimize the sol-gel surface preparations processes and ease transition to end-users. Significant effort was put into evaluating kitting concepts for the Boegel-EPII chemistry. Although the commercially available four-component kits are relatively easy to use, kits with fewer components are desirable since they would simplify the process and reduce the chances of improper mixing. Several configurations for two- and three-component kits were evaluated for performance and shelf-life stability. The results demonstrated the feasibility of two-part kits; these will likely be introduced once proper

packaging schemes are identified and validated. In addition: 1) simplified mixing procedures were validated for the four-component kits in order to save time; 2) the use of a surfactant to improve coating uniformity and appearance was evaluated; 3) a simple garden sprayer was identified for inclusion in kits for use in applying the mixed solution as an alternate to brushing; and 4) the pot-life of the mixed solution was determined to be at least 10 hours.

Quality control issues were also addressed during the effort. In one study, the amounts of each component in the formulation were varied and performance effects were documented. In another, the incorporation of dye into the basic Boegel-EPII solution was investigated since this would greatly improve the ability to visually inspect surfaces for proper coating application. Unfortunately, an acceptable dye was not identified. Finally, in order to better understand the adhesion mechanisms and optimize the sol-gel processes, the nature of applied coatings and pretreated metal surfaces were studied.

7.6 Future Work

SERDP Project PP-1113 developed viable surface treatments for metal adhesive bonding for a variety of applications. Although limited implementation has occurred for specific applications, follow-on transition-related work is required for widespread implementation. Most of this relates to moving a laboratory process to the end-users' environments. Tasks required include: 1) establishing sol-gel drying time for a range of temperature/humidity cases; 2) validating quality control and kitting concepts; and 3) conducting testing beyond coupon level, including fatigue and additional moisture-exposure tests such as outdoor exposure and stress durability in a hot/wet environment. Input from end-users who formed a key part of the development team indicates there are no significant roadblocks to successful implementation for both depot and field-level adhesive bonding applications. Transition issues are being addressed by the SERDP Project PP-1113 team, expanded to include additional end-users, via ESTCP Project PP-0204.

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APPENDIX

DRAFT GRIT-BLAST/SOL-GEL PROCESS

Materials

- Solvent (MEK or acetone)
- Rubber gloves (to conform to applicable safety regulations)
- Dust mask (to conform to applicable safety regulations)
- Goggles (to conform to applicable safety regulations)
- Respirator (to conform to applicable safety regulations)
- Clean, lint-free wipers (Duralace® 9404 Aerospace Wipes (NSN 7920-01-180-0557) or equivalent)
- Nitrogen (dry and oil-free) or certified clean, dry air
- 3-inch Scotch-Brite™ Roloc™ Surface Conditioning Discs, 3M Company (for high-speed grinder; very fine)
- Aluminum-oxide grit (50-63 micron, white)
- AC-130 sol-gel kits (Advanced Chemistry and Technology)
- Natural bristle brush (such as camel's hair)
- BR 6747-1 adhesive primer (Cytec Engineered Materials)

Equipment

- High-speed grinder
- Grit blaster
- HVLP spray gun (optional for sol-gel)
- HVLP or conventional air spray gun (for adhesive primer)
- Color standards to measure primer thickness or eddy current thickness gauge (such as Isoscope)

NOTE

This process is based on a controlled temperature and humidity laboratory environment.

1. Solvent wipe an area extending a minimum of 2 feet in all directions around the area to be prepared for bonding with one of the following solvents: methylethyl ketone (MEK) or acetone. The above list is order of preference. Choose a solvent that is approved at the application location. Continue until no residue appears on a clean Duralace® wipe.

2. Remove all surface coatings (organic and inorganic) down to bare metal using locally-approved procedures. Remove coatings in an area that exceeds the bonding area in all directions by at least one inch and preferably two inches.

3. Solvent wipe the bond area (at least 4 inches in all directions beyond the edge of the bond area) using wipes moistened with MEK or acetone. Wipe until all residue is removed (new wipes remain clean after wiping). Be careful not to drag contaminants into the bond area from the surrounding structure. On the last wipe, remove the solvent with a second clean wipe prior to its evaporation.

4. Connect high-speed grinder to oil-free nitrogen or clean, dry air and abrade the area to be prepared using a new 3-inch Scotch-Brite™ Roloc™ disc (very fine grit). Abrade to a uniform surface.

5. Solvent wipe the bond area per directions of Step 3. Time between final solvent wipe and grit-blast step shall not exceed 60 minutes.

6. Mix AC-130 per the kit procedures. The induction time for the sol-gel solution is 30 minutes. The pot life of the mixed solution is 10 hours after induction time is complete. Clearly label the sol-gel solution with the allowed application period or pot-life (time from completion of step 5 plus 10 hours).

7. Grit blast an area one inch in all directions greater than the bond area with 50-63 micron aluminum oxide grit using 30-80 psi *oil-free nitrogen or clean, dry air* pressure. Slightly overlap blast area with each pass across the surface until a uniform, fine matte finish is attained. Overlap blast area with each pass across the surface until a uniform matte appearance has been achieved.

8. Remove as much excess grit from the bond area as possible by blowing off with dry, *oil-free nitrogen or clean, dry air* then remove the grit containment arrangement. All grit will not be removed from the surface. Sol-gel should be applied as soon as possible after grit-blasting. The time between grit-blasting and sol-gel application shall not exceed 120 minutes.

9. Apply sol-gel in one of the two following manners:

    A. *Brush Application:* Rinse a clean natural bristle brush with distilled or deionized water and use it to apply the sol-gel solution. Apply a thin film of the solution to the grit-blasted surface and check for "water breaks." If water breaks occur, restart the process at Step 3. If the surface is water-break-free, continue to apply sol-gel solution to the surface to maintain a film of solution on the surface for a 2-3 minute period. Brush the sol-gel from the center toward the edges of the bond area. Do not allow the surface to dry during the entire application process. The solution will pick up grit from the surface as the brush is continually dipped into the mixture.

    B. *Spray Application:* Apply sol-gel solution by spraying onto the metal surface with an HVLP gun. If "water" breaks occur, restart the process at Step 3. If water-break-free, keep the surface continuously wet with the solution for 2-3 minutes. Do not allow the surface to dry during the entire application process.

10. After the 2-3 minute wet time has elapsed, allow the surface to dry for a minimum of 60 minutes and a maximum of 120 minutes at ambient conditions. If possible arrange the part so that the solution will drain freely. Primer must be applied within 120 minutes after the initial sol-gel application.

11. Connect primer spray gun to dry, *oil-free nitrogen or clean, dry air* and spray BR 6747-1 adhesive primer onto the prepared bond area to obtain a cured film thickness of 0.0001 to 0.0003 inches (0.1 to 0.3 mil). Color standards may be used to check primer thickness prior to cure. This is difficult since the color of the cured primer differs somewhat from the uncured condition. Color standards using uncured primer sprayed on grit-blasted panels prepared by the above procedure must be used. In any case, the cured primer thickness must be measured (Step 14).

12. Allow primer to dry at ambient conditions for a minimum of 30 minutes and a maximum of 60 minutes prior to heat cure.

13. Cure the primer for 60 $\pm$5 minutes at 250°F $\pm$5°F. There is no need to maintain a controlled ramp rate. Once the primer is fully cured and bonding surface has cooled to 90°F or lower, adhesive may be applied and cured.

14. Verify cured adhesive primer thickness using a color standard or eddy current thickness gauge calibrated for the 0.1 to 0.3 mil range. Color standards must be made (with verified thicknesses) on a grit blasted surface prepared as outlined above. If the cured primer thickness is not in the acceptable range, the process must be restarted at Step 2.